

Supported palladium catalysts in environmental catalytic technologies for gaseous emissions

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Abstract

Palladium is the active component in several catalytic formulations for environmental technologies, due to its superior performances in the conversion of some hydrocarbons (for example, methane) and halocarbons, and the thermal stability and low volatility of Pd species. The properties and reactivity of Pd-based catalysts in the conversion of methane catalytic combustion for gas turbine applications, reduction of greenhouse gas (methane, N₂O) emissions, hydrodehalogenation and oxidative destruction of halocarbons and their applications in the elimination of other pollutants from gaseous emissions are reviewed, with emphasis on the structure-activity relationships, reaction mechanism and sensitivity to poisoning. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Palladium is extensively used as the active component in several industrial catalytic formulations for the conversion of environmentally unfriendly chemicals in gaseous emissions. Like platinum, palladium shows low light-off temperatures in the oxidation of hydrocarbons and other organic chemicals [1–5]. The activity of palladium is generally better than that of platinum in the conversion of methane, but its activity is less in the transformation of other chemicals [1–5]. The resistance of palladium to thermal and hydrothermal sintering is also better than that of platinum [6], but its behavior in the presence of poisons, such as sulfur containing pollutants [3,7] or lead [8] is worse.

While palladium was cheaper than platinum in the past, and therefore, cost was a relevant factor in

determining its practical applications as well as relative research (for example, considerable attention was given to the development of Pd-only catalysts for automotive applications in the past [9,10]), the difference in cost no longer exists. Therefore, today the choice of Pd as the active component rather than Pt is essentially determined on the basis of performance and stability considerations.

The largest use of Pd in catalytic applications for cleanup of emissions from stationary sources is in the field of catalytic total oxidation of hydrocarbons [11,12]. Several types of practical applications have been investigated in the past, including hydrocarbon removal in enclosed environments and odor control, removal of volatile organic compounds (VOCs) formed in polymer processing, coating operations, spray painting and offset printing, domestic and other heating systems, industrial boilers and gas turbines. Compared to platinum, the higher thermal stability of palladium makes it the preferable choice for high

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temperature applications, such as catalytic combustion in boilers and gas turbines [11,12], and its higher activity in CO and CH₄ oxidation makes it the choice for use in catalysts for low temperature conversion of these components [13–15].

Other well studied types of applications of Pd-based catalysts in recent years include NO reduction by CH₄ in the presence of O₂ [16–18] and destruction or conversion to less harmful chemicals of chlorinated hydrocarbons [19–21]. More specific types of applications are the removal of ethane from fruit storage areas, in order to avoid ripening of the fruit [22], removal of ozone and other gaseous pollutants in ambient air [23], catalytic combustion of gasified biomass [24] and elimination of ammonia present in biofuels [25,26], decomposition of N₂O [27] and catalytic combustion of odors in domestic space [28]. Either supported Pd catalysts or Pd-zeolite catalysts are used in these applications.

The state of the active Pd component in these various applications is a determining factor in regard to performance. Recent aspects and evidence regarding this question are thus, analyzed here first before discussing more specifically the performances and reaction mechanisms of Pd-based catalysts in the reactions cited above. The catalyst stability and sensitivity to poisoning are also discussed, their being a central problem for the application of Pd-based catalysts in the reduction of the environmental impact of gaseous emissions.

2. Catalytic combustion for gas turbine applications

Catalytic methane combustion for gas turbine applications has recently reached a commercial demonstration stage [29,30]. Catalytic combustion offers the possibility of reducing NO_x emissions to 1–2 ppm, i.e. even lower than is generally feasible with SCR (selective catalytic reduction) after-treatment technology using ammonia as reductant, at lower cost and avoiding at the same time the ammonia slip and other drawbacks of SCR technology. Other advantages include low (few ppm) emissions of unburned hydrocarbons and CO, and reduced problems of combustion instability and consequent noise. A demonstration unit equipped with Catalytica XONON[®] technology

[31] is in operation currently to demonstrate 8000 h durability under industrial operations. The catalyst section of the XONON[®] combustor (which is the first stage of the three stages forming the XONON[®] combustor; in the other two the reaction proceeds in homogeneous phase) consists of a palladium-based active washcoat deposited onto metallic monoliths.

The choice of palladium as the active component derives from both its chemical and reactivity properties [29]:

1. Higher activity in the combustion of methane, which results in a low light-off temperature, as has been recognized for a long time [32].
2. Unique capability of temperature self-control associated with the PdO–Pd reversible transformation [31,33,34]. The adiabatic reaction temperature in natural gas combustors may exceed 1300°C causing quick deactivation of almost all catalysts [11]. The PdO spontaneously reduces to metallic Pd above 800°C and metallic Pd is less active in methane combustion than PdO. The transformation is reversible, and therefore, this property is an effective way to chemically control the surface temperature of the catalyst and prevent fast deactivation.
3. Low volatility of Pd species (metal, oxides, hydroxides and oxyhydroxides) under thermal and hydrothermal conditions [11].

2.1. State of Pd during catalytic reaction

The PdO/Pd transformation and the consequent change in surface reactivity is a relevant characteristic of Pd-based catalysts for methane combustion. Therefore, numerous studies has been focused on this question.

Decomposition of PdO occurs through three transitions, two major and one minor. The temperature depends on the partial pressure of oxygen. For a 1% O₂ concentration in the reacting atmosphere, these transitions are centered at about 720, 760 and 840°C, respectively (Fig. 1a) [33,34].

During the cooling ramp, O₂ uptake due to reformation of PdO starts markedly at lower temperatures (for a 1% O₂ atmosphere, onset of the transitions occurs at about 500°C with the maximum centered at 430°C, Fig. 1a). Oxygen uptake in this step is lower

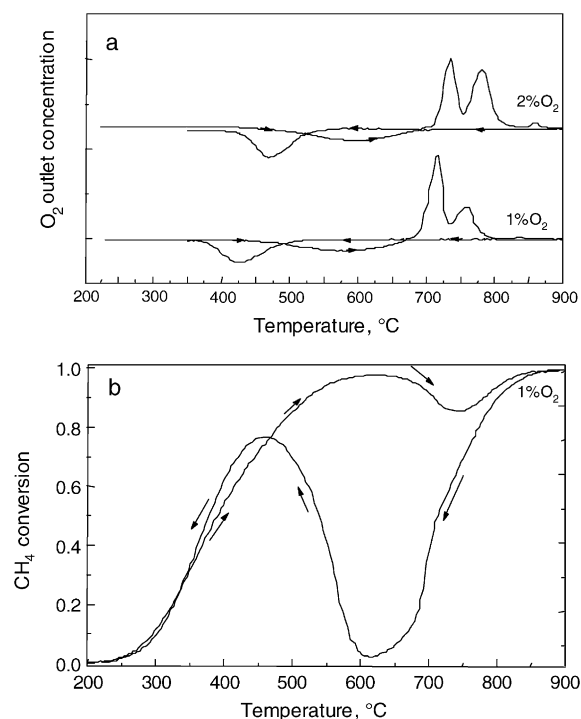


Fig. 1. (a) Temperature-programmed oxidation profiles on 10% w/w Pd dispersed on a La₂O₃-stabilised Al₂O₃ support at $P_{O_2} = 0.01$ and 0.02 bar. (b) Behavior of the same catalyst in methane temperature-programmed combustion profile at GHSV = 10⁶ h⁻¹ using a structured annular reactor. Elaborated from Groppi and coworkers [33,34].

than oxygen released during the first decomposition step, but in a further run a broad oxygen uptake peak is observed in the 550–650°C temperature range, indicating that further palladium reoxidation occurs at higher temperatures after the first step of PdO_x formation. A complex chemistry of PdO decomposition and Pd reoxidation is, thus present.

The onset temperature of the decomposition steps of PdO depends on the oxygen partial pressure [35]. A linear relationship between $\ln(P_{O_2}^{0.5})$ versus $1/T$ (where T is the onset temperature of the transition) is observed, in good agreement with data for decomposition of bulk PdO [36]. Furthermore, decomposition did not start at lower temperatures than the onset temperature (Fig. 1). Both data were interpreted on the basis that the decomposition process is thermodynamically driven, although it may be noted that often in the solid state kinetics studies the presence of a long induction

time (related to the nucleation period, see below) was observed and no apparent reaction was observed below a threshold temperature due to this nucleation mechanism. Therefore, the question of the presence of a kinetically or thermodynamically controlled reaction of decomposition of PdO should be reconsidered. In agreement, it has been observed that using alumina doped with lanthanide ions as the support for palladium, the onset of the decomposition steps is influenced, although less markedly than the onset of the temperature of the reoxidation step [29]. Also using different types of supports, such as zirconia, the decomposition temperature of PdO changes. These data are not in favor of a thermodynamically controlled decomposition reaction.

The apparent activation energy derived for the first and second decomposition transitions is different [33,34]. With increasing oxygen partial pressure, the oxygen release in the second transition increases at the expense of that released in the first transition. These data suggest that the two decomposition transitions are related to different PdO_x species which, however, may transform into each other (reversible in series process $Pd \rightleftharpoons PdO_{x1} \rightleftharpoons PdO_{x2}$), with the species associated with the higher decomposition transition (PdO_{x2}) characterized by a higher value of x in PdO_x ($0 \leq x \leq 1$). The relative amounts of oxygen released in the two decomposition steps depend not only on the O₂ partial pressure, but also on the sample history and conditions of pretreatment at lower temperatures [33,34]. These data are consistent with the hypothesis of the reversible in series process, and provide further indication that the idea of a thermodynamically driven decomposition process is probably not correct.

A third decomposition step is also sometimes observed at high temperature (Fig. 1a), but it is of minor importance (not more than 1–5% of the intensity of the other decomposition peaks) and probably associated with isolated Pd ions on the surface [37].

The hysteresis between PdO decomposition and Pd reoxidation has been attributed to a limiting temperature of Pd to chemisorb O₂ [35] or to the formation of a passive layer of chemisorbed oxygen [38]. Both interpretations are not fully convincing, because they do not explain, for example, the dependence of the hysteresis on the nature of the support. Voogt et al. [39] studied quantitatively the process of oxidation of Pd particles supported on SiO₂/SiO(1 0 0) by XPS and

found that the rate limiting step in the process is the lattice reconstruction needed for the formation of a new oxide layer at the oxide–metal interface. However, the data were limited to a maximum of 500°C, and therefore, extrapolation to the higher temperature range of interest for methane catalytic combustion, may not be correct. In fact, a recent TEM study of the microstructural modifications of an alumina-supported palladium combustion catalyst [40] showed that oxidation during cooling in air from high temperature did not occur via a shrinking core mechanism. The oxide formed under these conditions showed significant roughening which may explain the presence of a hysteresis (related to the mechanism of nucleation and oxidation, see below) and the dependence on the nature of the support (interaction between the support and the palladium particles alters the mechanism of nucleation). No evidence has been found by TEM for the presence of different PdO_x species, suggesting that the two possible PdO_x species discussed above may be related to different thicknesses of the oxide layer on palladium particles and possibly different roughness more than to different types of species (such as crystalline and amorphous species).

High temperature XRD data [33,34] indicate only one type of crystalline PdO the amount of which corresponds to that determined using temperature-programmed methods (TG, TPO). This indication suggests the absence of amorphous PdO_x as earlier indicated [35]. Rietveld refinement of XRD data [33,34], however, indicates the possibility of the formation of intermediate amorphous PdO_x in the PdO to Pd transformation and the different dimensions of the particles which is not consistent with only the expected larger particle size of PdO with respect to Pd due to oxygen. Therefore, redispersion/sintering phenomena occur at the same time as the redox Pd/PdO transformation processes, in agreement with TEM data [40].

When the lanthanide content in the support is high, such as in ceria–zirconia mixed oxides, encapsulation of metal Pd particles by the support may also occur [41,42]. Encapsulation favors the fcc structure of Pd particles. This mechanism may also partially occur on lanthanum-ion stabilized alumina or zirconia (lanthanum ions are used to improve the hydrothermal stability), and thus explains the influence of the support on the hysteresis of the PdO → Pd → PdO transformation. Garbowski et al. [43] noted that the

reduction of PdO/Al₂O₃ by H₂ at 500°C leads to the formation of Pd particles with an enhanced presence of the Pd(1 1 1) surface due to the epitaxial stabilization by the Al₂O₃(2 2 2) surface. Rodrigez et al. [44] using a controlled atmosphere electron microscope also found that the nature of the Pd which forms by decomposition of PdO depends on the stabilization effect of the support. More recently, Lyubovsky et al. [40] also using high-resolution transmission electron microscopy observed that small Pd particles formed upon decomposition of PdO are mobile over the surface and progressively grow to larger particles which surprisingly show higher activity notwithstanding the lower surface area. This derives from a restructuring of the Pd metal particles with preferential exposure of low-index surfaces which are more active.

The process of sintering and restructuring of Pd particles clearly depends on the support and determines the temperature of onset of reoxidation, thus explaining the dependence of the activity and hysteresis on the support. Crozier and Datye [45] used in situ electron microscopy to study the reduction of PdO to Pd and noted that at temperatures below 500°C the reduction proceeds via the formation of a thin metal shell surrounding an oxide core with the rate determined by oxygen diffusion through the metal shell. An ordered structure is, thus found and the volume change associated with the phase transformation leads to the formation of central voids in the particles. At higher temperatures, the voids are not detected indicating that cracks and pits form which determine a change in the mechanism of reduction. Cracks and pits were detected on the surface of the crystallites during Pd oxidation [46]. It was also suggested that the nucleation of PdO over Pd catalyzes the further oxidation of the particles (see below) [33,34].

It may be concluded that the redox process of PdO → Pd → PdO transformation in the 700–900°C temperature range (that relevant regarding the behavior of Pd-based catalysts for methane combustion) is not simple as may be expected. It also should be noted that the transformation is different from that detectable at lower temperatures and governed mainly by bulk diffusion phenomena. The difference is determined by the presence of defects which modify the mechanism of transformation as well as by the presence of fast mobility of species which induce fast possible reconstruction and sintering/redispersion

phenomena. All these effects depend on the interaction between the Pd particles and the support. This determines the sensitivity of this transformation to the nature of the support and in turn, the catalytic reactivity, while different results (or dependence on the nature of the support) are expected for lower temperatures applications.

2.2. Active sites of palladium in methane combustion

The discussion in the previous section has evidenced that the redox chemistry of the $\text{Pd} \rightleftharpoons \text{PdO}$ transformation is not fully understood and that a different distribution of species may exist depending on the history of the sample pretreatment and reaction conditions (temperature at the catalyst surface and feed composition). As a consequence, no definitive indications have been reported in the literature about the relationship between palladium species and reactivity in methane combustion. Lyubovsky and Pfefferle [47] noted also that the catalytic activity data were extremely scattered, with turnover frequencies being different by as much as three orders of magnitude and activation energies also being different by a factor of three.

In general terms, in the high temperature region (500–900°C), when the temperature is increased, the conversion of methane increases up to a maximum after which it decreases in correspondence to the threshold value for the onset of the first PdO decomposition (Fig. 1b). This minimum in activity can be detected only for very high space-velocities (above 1 million l/kg h [33,34]). The CH_4 conversion passes through a minimum around 750°C and then increases again. By decreasing the temperature from 900°C, a deep minimum in the CH_4 conversion is found around 620°C, and thus for a temperature lower than the minimum during the heating ramp for increasing temperatures. With further decreases in temperature, the conversion of CH_4 increases up to a maximum of around 450°C and then decreases again as temperature decreases. This behavior is consistent with the idea that PdO is the active species and Pd metal is inactive or much less active, although (as discussed later) other authors [47] suggest instead that the relative order of activity between PdO and Pd depends on the reaction temperature.

A further problem derives from the fact that various palladium species have been identified to be present

(see Section 2.1) the relative amounts of which depend on various factors. Therefore, the catalytic behavior in high temperature methane combustion cannot be simply related to the presence of the $\text{PdO} \rightleftharpoons \text{Pd}$ equilibrium. In agreement, a closer comparison of reactivity and oxygen uptake/release data (Fig. 1) indicates a deviation from the classical Arrhenius trend below the onset temperature of PdO decomposition. Furthermore, during cooling, reformation of minor amounts of PdO is sufficient to completely restore activity (Fig. 1) [33,34].

Groppi and coworkers [33,34] suggested the presence of a highly O-defective PdO or sub-stoichiometric PdO as intermediate in the reoxidation process and that this species contributes to a major extent to the overall methane combustion activity. Furthermore, in agreement with Iglesia et al. [15], they suggested that methane combustion occurs through a dual site mechanism involving a reduced site (an oxygen vacancy in the PdO lattice) promoting dissociative adsorption of methane and an oxidized site that provides oxygen. These hypotheses explain the behavior in methane combustion discussed in reference to the data shown in Fig. 1.

A synergetic interaction between PdO and Pd, or between the two PdO_x species (depending on the nature of the support and history of pretreatment, as discussed in the previous section) are, thus the factors determining the catalytic behavior according to these authors [15,33,34]. However, other literature data indicate that identification of the nature of the active palladium species probably requires more studies.

Eguchi et al. [48], studying $\text{PdO}/\text{Al}_2\text{O}_3\text{-MO}_x$ (where M: Co, Cr, Cu, Fe, Mn and Ni) catalysts observed that activity is related to the adsorption state of oxygen on palladium. The activity increases when the amount of adsorbed oxygen increases due to the effect of the second transition metal. Müller et al. [49,50] investigated PdO/ZrO_2 catalysts prepared from Pd/Zr glassy metals and suggested that the support has a negative role. Large particles of PdO, which show a reduced interaction with the support, were found to be more active. The reaction mechanism was found to follow a simple Mars–van Krevelen mechanism of PdO reduction by methane and Pd reoxidation by O_2 .

Bell et al. [51] in a comprehensive and detailed investigation on the dynamics of Pd oxidation and PdO reduction by H_2 and CH_4 in PdO/ZrO_2

catalysts, found that during oxygen uptake a monolayer of oxide forms instantaneously, while further oxidation proceeds slowly by progressive increase in the oxide shell around a Pd metal core. The thickness of this oxide shell depends on the temperature. The initial oxide layer is amorphous, while progressive crystallization of the oxide layer occurs with the increase in the shell thickness. The dynamics of the process follow the Cabrera–Mott theory for metal oxidation in thin films. Electrons from the metal are assumed to tunnel through the thin oxide layer and react with adsorbed oxygen atoms to form oxygen anions. The surface charge electric field drives the anions towards the oxide–metal interface. The process is, thus initially very fast and then becomes progressively dominated by diffusion. It is interesting to note that the diffusion process should depend on the surface electric field which in turn depends on the metal to support interaction (which determines the surface charge on the metal). It is, thus reasonable that this process depends considerably on the type of support, as effectively observed in the literature.

Bell et al. [51] suggested instead that the reduction of PdO by CH₄ occurs via an autocatalytic-nucleation mechanism which is outlined in Fig. 2. Small particles of Pd first form on which CH₄ can dissociate. The fragments (H and CH_x) diffuse to the metal–oxide boundary where reduction of the oxide occurs. An induction period is, thus observed before rapid reduction occurs. The rate of reduction also changes: it is initially first order in the amount of Pd formed and then becomes zero order in metallic Pd. Using H₂, different reduction kinetics are instead observed which

follow a more classical shrinking core mechanism (Fig. 2). The nucleation kinetics for the reduction of PdO by methane may also explain the previous observations interpreted instead as proof for the presence of a synergetic PdO_x/Pd interaction in methane combustion (see above).

2.3. Oscillations in catalytic activity in relation to dynamics of palladium redox changes

The presence of a complex redox pattern of PdO/Pd transformation and of induction times as well as of autocatalytic effects in this transformation indicates the possibility of oscillations in the catalytic activity in methane oxidation in supported Pd catalysts. Non-isothermal oscillations in methane were in fact observed under oxygen deficient conditions [52–54]. The oscillations are characterized by an induction time and thermal (low frequency) oscillations in the temperature of the catalyst bed. The frequency is higher for a lower mass of packed catalyst bed, in agreement with that found in other cases of non-isothermal oscillations [55]. This indicates that the oscillations probably do not depend on the dynamics of in situ reconstruction of palladium particles, but rather to the presence of thermal patterns deriving from the specific kinetics of methane oxidation. The absence of detailed studies on this question, however, make further clarification of this question impossible. It may be noted that Euzen et al. [56] instead associated the oscillating behavior of methane conversion to the redox PdO/Pd transformation, although clear proof is not available. They also noted that the nature of the support is a

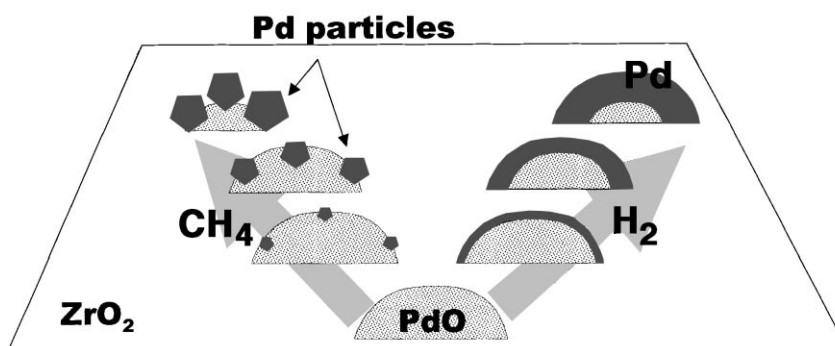


Fig. 2. Cartoon of nucleated reduction of PdO by CH₄ and shell-wise reduction of PdO by H₂. Elaborated from Bell et al. [51].

critical factor for the presence of oscillations in catalytic activity.

Oscillations in catalytic activity have also been observed during CO oxidation on PdO/Al₂O₃ [57]. In this case, the region of the self-sustained oscillations in CO conversion was related to the presence of two parallel mechanisms, a radical pathway of oxygen activation by Pd⁺ to form O₂ anion-radicals and a redox mechanism of oxygen interaction with Pd clusters to form Pd²⁺O₂ complexes and surface oxide (Pd²⁺O²⁻). This double pathway was supported by FTIR data. The oscillations were related to phenomena of surface reconstruction of palladium species and associated change in the pathway of oxygen activation. It is not clear how oscillations may be described from this mechanism and what is the driving force determining dynamic reconstruction of palladium particles. Other aspects not considered are the question of the surface coverage of palladium particles by CO and O₂ and the kinetics of reduction/reoxidation of palladium particles.

The questions of the possible relationship in the mechanism of oscillations for methane and CO oxidation on PdO/Al₂O₃ and how the metal/support interaction modifies this mechanism have also not been considered. For both methane and CO oxidation, for example, it has been noted that the addition of Ce to PdO/Al₂O₃ has a comparable influence on the presence of oscillations in activity [54,57], indicating that common aspects in the mechanism of oscillations should be present. Oscillations in both cases were observed at low temperatures (below 500°C), however, the presence of Ce inhibited the hysteresis of the PdO/Pd transformation [57]. This indicates that there is a relationship between the phenomena responsible for oscillations in the catalytic behavior and redox PdO/Pd changes at high temperature.

Although very limited data exist in the literature about these questions, the indications discussed point out that a better investigation of these phenomena and of the chemistry and dynamics of transformation in both high and low temperature methane oxidation on Pd supported catalysts is necessary to clarify the reaction mechanism and the factors controlling it.

It has been recently reported [47], in contrast with the well accepted idea that Pd is less active than PdO (basis of the chemical thermostat effect cited in the previous section and applied in the XONON[®]

combustor), that metallic Pd is more active towards methane oxidation than the oxidized PdO form at high temperature, while the contrary happens at low temperature, because the activation energy for methane oxidation over PdO is about 18 kcal/mol, and about 35–40 kcal/mol over the Pd phase. Lyubovsky and Pfefferle [47] noted, however, that the pre-exponential factor for these reactions depends strongly on the process conditions and the history of pretreatment. For this reason, the pre-exponential factor may also change during reaction and can be the cause of oscillations in activity.

These observations put further question marks on the identification of the relationship between nature of the palladium phases and reactivity, and between dynamics of transformation and oscillations in catalytic behavior. This problem is of critical importance for the development of catalytic combustors for methane oxidation (including their correct mathematical modeling) as well as catalysts for low temperature methane oxidation (see Section 2.4), and further effort in clarifying these aspects is necessary.

2.4. Deactivation and sensitivity to poisoning

Stability of the catalyst is clearly a determining factor for industrial application. Durable catalysts [11] must be able to resist: (i) deactivation by sintering; (ii) loss by vaporization; (iii) deactivation by corrosion (by contaminants brought in by airborne dusts — Si, Al, Cl — or oil particles — S, P); (iv) thermal shock; and (v) erosion and delamination. These requirements put severe limitations on the type of materials which may be used in catalytic combustors. The best combination of properties is usually offered by Fe–Cr–Al metallic monoliths coated with a lanthanide-supported alumina washcoat (lanthanum ions promote stability of alumina, but also have a stabilization effect on palladium dispersion [59]), onto which around 10% wt. The Pd is deposited [29,30,58]. Other interesting supports for palladium are hexaaluminates [12] and zirconia [48]. Pilot plant durability tests of methane catalytic combustors show good resistance to deactivation of this kind of catalysts [29–31], provided that the catalyst surface temperature does not exceed about 900–950°C. Specific scientific studies on the stability of supported Pd catalysts towards thermal or chemical deactivation, however, are limited.

The deactivation behavior of palladium-on-stabilized alumina was studied by Euzen et al. [56] both in laboratory and pilot plant apparatus. Results indicate that using a support calcined at high temperature (1230°C, to avoid further support sintering) the deactivation is mostly correlated to the metal transformation and PdO sintering. However, the activity dropped more steeply in relation to the appearance of metallic Pd.

The sensitivity to poisoning at high temperature of Pd-based catalysts has not been investigated in detail in the literature, but Geus et al. [60] observed that water (a product of reaction) inhibits the reaction rate (apparent order of reaction -0.8). The reason for this enhanced inhibition effect is not clear, but it seems not to be attributable to only a competitive chemisorption effect. Probably, water also influences the redox properties of palladium and in turn the catalytic activity. However, more specific studies are necessary to clarify this question.

3. Palladium catalysts for the conversion of greenhouse gases

The Kyoto agreement on the reduction of greenhouse gas (CO_2 , CH_4 , N_2O and chlorofluorohydrocarbons) emissions has renewed interest in catalytic technologies to reduce emissions and in particular those of non- CO_2 greenhouse gases (NCGG) [61], because the reduction of CO_2 mainly requires an improvement in the efficiency of production and use of energy more than catalytic technologies for the conversion of CO_2 which have been estimated to have only a marginal effect on the worldwide CO_2 balance.

The greenhouse gases are characterized by different concentrations in the troposphere and life times. Their greenhouse effect, therefore, should be evaluated in terms of global warming potential (GWP) over a time period of usually 100 years [61]. Methane and N_2O each contribute to about 8–9% of the GWP. Therefore, their contribution is relevant and their emissions should be limited. About half of their emissions is from natural sources and furthermore some anthropogenic emissions also cannot be controlled. Reduction of the emissions of CH_4 and N_2O , thus requires achieving a high efficiency of removal on the emissions which effectively can be controlled. Palladium-based

catalysts play an important role in developing these technologies for the reduction of greenhouse gas emissions.

3.1. Methane

There are three main relevant cases requiring the development of Pd-based catalysts to reduce methane emissions: (i) conversion of residual methane in the emissions from lean burn natural gas vehicles (NGVs); (ii) conversion of methane and other noxious components in the emissions from sewage disposal and water treatment plants; and (iii) conversion of methane in the emissions from mining activities [61]. The combustion of gases produced from biomass anaerobic digestion is not included, because in this case the heat of combustion is high enough to maintain autothermic operations also at high temperatures (typically above 450°C). Activity at low temperature, therefore, is not a determining factor for the choice of catalyst, while in the three applications cited above a very low light-off temperature (200°C or below) is a demanding requirement. Furthermore, the methane concentration in all three cases is low, typically less than 1–2%.

The only cases reported in detail in the literature are the conversion of residual methane in the emissions from NGVs. There are little data on catalytic technologies for the conversion of methane in the emissions from sewage disposal and mining activities, although about half of the anthropogenic methane emissions (about 380 Mt per year) can be associated to them [61]. However, the basic problems in catalyst development are common to those of catalysts for the treatment of the emissions from NGVs, and therefore, the discussion of the catalysts for these emissions is also relevant to catalysts for the other two cases.

Lean burn NGVs equipped with catalysts are commercially available in buses and other fleet service vehicles. The advantages of these engines are: (i) very low particulate emissions; (ii) lower nitrogen oxide emissions than for vehicles using a stoichiometric air to fuel ratio (all cars mounting three way catalysts) due to cooler combustion resulting from the high air to fuel ratio; and (iii) better fuel economy. Non-methane hydrocarbons (NMHCs), CO, and oil derived particulate in the NGV exhaust can be reduced to current legislation requirements by using

a conventional monolithic oxidation Pd–Pt catalyst. However, the methane emissions are above allowed limits and are reduced minimally by the conventional catalyst.

Characteristics required by a catalyst for methane conversion in lean burn NGVs are: (i) low light-off temperature (200–300°C or below) at space-velocities of 50,000 h⁻¹ or above; (ii) high efficiency using low methane concentrations (below 1000 ppm) and high oxygen concentrations (the air to fuel ratio in lean burn engines is typically in the 20–27 range, and thus residual oxygen in exhaust gases may be 8% or higher); (iii) stability (thermal and hydrothermal) in the presence of about 8% O₂ and similar water concentration in the feed; and (iv) resistance to deactivation by sulfur (low concentrations of sulfur compounds are present as impurities in the feed).

The Pd-based catalysts show the best performances under the conditions outlined above, but are very sensitive to poisoning by H₂O and SO₂ (the latter as little as 1 ppm SO_x in the exhaust vehicle gases) [13,62,63] which shift the light-off curve to temperatures about 200°C higher. Furthermore, high Pd loadings in the catalysts are necessary. The performances of the catalysts are, thus still not satisfactory and further improvements are necessary.

Three directions of research may be identified to improve performances: (i) identification of the reaction mechanism of methane activation as a tool to design

improved catalysts; (ii) identification of the mechanism of deactivation to identify how to prepare more resistant catalysts; and (iii) study of alternative types of supports for palladium which may improve activity or stability.

3.1.1. Mechanism of methane activation

The problem of the factors determining low temperature methane oxidation on supported Pd samples was analyzed by Iglesia et al. [15] using PdO_x/ZrO₂ catalysts. They observed that the rate of methane oxidation at low temperature (280°C) is first order with respect to methane and zero order with respect to oxygen, with an inverse dependence on water concentration. The reaction mechanism proposed to interpret these data (although other interpretations are possible) is summarized in Fig. 3.

The rate determining step is the dissociative chemisorption of CH₄ on a site pair consisting of adjacent Pd surface vacancies and surface Pd–O species. The negative water effect is due to the inhibition of the formation of Pd–O species which in turn inhibit the desorption of water during recombination of the surface hydroxyl groups.

The catalytic sequence of Fig. 3 suggests that stronger Pd–O bonds in small PdO clusters or incompletely oxidized PdO_x crystallites can lead to a lower surface density of vacancies, and thus to lower methane oxidation turnover numbers. The authors,

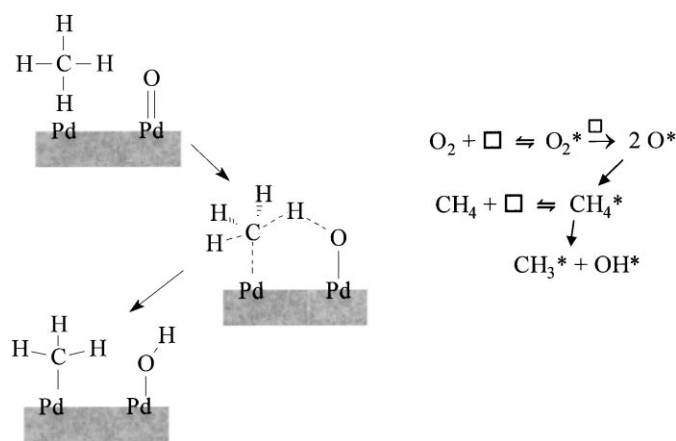


Fig. 3. Proposed mechanism of methane dissociation on a surface Pd–PdO site pair on PdO_x crystallites and relative kinetic mechanism. Elaborated from Iglesia et al. [15].

thus concluded that small PdO_x crystallites and PdO_x samples which have undergone decomposition to Pd metal or transformation to oxygen-deficient Pd oxides are less active in low temperature conversion of methane.

For similar catalysts, Epling and Hoflund [64] proposed instead a different reaction mechanism on the basis mainly of XPS data. Methane activation occurs with the formation of a carbon species which bonds with surface O to form an adsorbed CO species (how, is not described), further converted to carbonate or bicarbonate species which decompose to CO_2 . This reaction is catalyzed by the bare support, but not by reduced Pd metal on alumina. The Pd metal, however, increases the rate of methane dissociative chemisorption. The species produced then migrates by spillover to the oxide support or Pd oxides, where it reacts. Due to the active role of zirconia supports, in contrast to alumina, PdO/ZrO_2 is more active at lower temperature than $\text{PdO}/\text{Al}_2\text{O}_3$. Epling and Hoflund [64] reported a 56% conversion of methane to CO_2 at 250°C for zirconia-based catalysts in contrast to 32% for alumina-based catalysts (5 wt.% Pd, space-velocity 18,600 $\text{N l/g}_{\text{ctz}} \text{ h}$). The authors also observed that mild oxidation and reduction treatments lead to improved catalytic performances.

Bell et al. [65] suggested instead a bifunctional mechanism for methane oxidation on PdO/ZrO_2 samples. In agreement with Solymosi et al. [66], they observed that metallic Pd dissociatively chemisorbs methane producing $\text{H}_{(\text{s})}$ and $\text{CH}_{x(\text{s})}$ ($x = 1-3$) species. The more active samples were those showing small amounts of Pd in close contact with PdO. The species produced by methane dissociation diffuse to the Pd/PdO interface where they reduce the oxide (metal-assisted oxide reduction). Reoxidation rapidly converts the metal back to the oxide, and therefore, under steady-state conditions and at low reaction temperatures the amount of metal Pd is low. The methane combustion turnover rate at low temperatures can be increased, however, by adding small particles of a metal able to dissociate methane, but which do not rapidly reoxidize as Pd.

Baiker et al. [49,50] studying PdO/ZrO_2 catalysts derived from a glassy Pd–Zr alloy instead indicated that the reaction mechanism of methane oxidation involves the reduction of PdO by methane and Pd reoxidation by O_2 following a Mars–van Krevelen

reaction mechanism. Results using ^{18}O labeled palladium oxide supported this interpretation, although in contrast with other results discussed above. These authors also observed that the specific activity of sites exposed on the surface of large palladium oxide particles is higher than for sites localized on smaller particles. This is consistent with the results of Iglesia et al. [15], even though there is a contrast in the mechanisms of reaction proposed by the two groups.

Burch et al. [3] proposed that the decomposition of palladium hydroxide (deriving from methane activation, as shown in Fig. 3) and breaking the surface OH bonds are the rate-limiting steps in methane activation on PdO, in contrast with Iglesia et al. [15] who proposed methane activation on oxygen vacancies of PdO. In propane conversion on $\text{PdO}/\text{Al}_2\text{O}_3$ catalysts Schmal et al. [67] also found that the formation of palladium hydroxide on the surface decreases the number of active surface sites. The model they proposed for the most active species corresponds to a “skin” of PdO over Pd.

No definitive conclusions can be derived from the studies on the reaction mechanism of low temperature methane oxidation to identify how to design promoted catalysts with low temperature light-off activity. It is surprising, however, that no data have been reported on the possibility to promote methane activation using a bifunctional mechanism of activation on metal and super-acid sites.

Notwithstanding the different ideas, a common observation is that methane activation is faster on metallic Pd or partially reduced Pd sites, although PdO also must be present at the same time. Reduced palladium species form by methane combustion, but their reoxidation is the fast. This rate of reoxidation should depend on the surface charge at metal particles and work function. Doping the support (dopant induced metal-support interaction) or non-faradaic electrochemical promotion (NEMCA effect) can be possibilities to control the surface potential at metal particles, and thus the rate of reoxidation, stabilizing the presence of reduced Pd species, and thus promoting low temperature activity. It is, therefore, in principle possible to induce promotion of low temperature activity of supported Pd samples, but new studies in this direction and on the mechanistic factors determining activity are required.

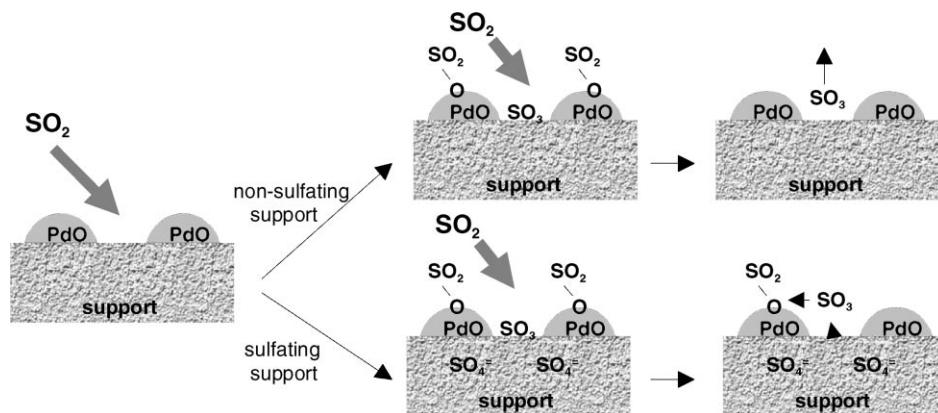


Fig. 4. Proposed mechanism for SO₂ inhibition of PdO methane oxidation activity for PdO on sulphating and non-sulphating supports. Elaborated from Farrauto et al. [13].

3.1.2. Mechanism of poisoning

Water shows a large inhibition, although reversible, on the low temperature activity of supported Pd catalysts, as discussed in the previous section, and has relevant implications also on the reaction mechanism. The effect derives from the slow rate of dissociation of surface Pd–OH species or their recombination with H₂O desorption. No indications have been reported on how to limit this drawback, but it seems probable that the support plays a relevant role. This is one of the reasons why zirconia allows more active samples at lower temperature than alumina.

Most of the studies have been focused on the effect of sulfur compounds on the behavior of Pd-based catalysts. Farrauto et al. [13] carried out an in-depth study of the problem and suggested the reaction mechanism for SO₂ inhibition of PdO methane oxidation activity which is outlined in Fig. 4.

The PdO converts SO₂ to SO₃. With a sulphating support, both the PdO and the support adsorb SO₃. During deactivation, the support acts as a sink for some of the SO₃, protecting the PdO (shielding effect). The adsorption of SO₃ decreases the rate and the degree of deactivation. When SO₂ is removed from the gas stream, the support spills SO₃ onto the PdO and continues the suppression of methane oxidation activity. Using a non-sulphating support, the shielding effect is not present (thus resulting in faster deactivation), but when SO₂ is removed from the gas stream, the initial activity can be restored. At a

temperature of about 600°C or above, in fact, SO₃ completely desorbs from PdO and desorption occurs even at low temperatures when methane is present.

This indicates that periodic regeneration may be possible during high load engine conditions (typical temperatures around 600°C). In the case of sulphating supports, however, it may be expected that reduction of the sulfate species will lead to the formation of H₂S instead of SO₂ with possible formation of PdS species [63], the regeneration of which is much more difficult.

McCormick et al. [62] observed that SO₂ causes both inhibition and deactivation for methane oxidation. The deactivation is partly reversible on PdO/Al₂O₃ at 460°C and completely reversible at 520°C. Also water was observed to show both inhibition and irreversible deactivation, the latter probably due to redispersion of the PdO particles. A synergetic interaction was also found between water and SO₂. When they are both present at 520°C, deactivation is faster than with either SO₂ or water separately and not completely reversible. Furthermore, previous exposure to SO₂ increases the sorption strength of water on PdO/Al₂O₃. McCormick et al. [62] hypothesized that this effect is due to the fact that water may force spillover of surface SO_x species from the alumina support to PdO, and enhance the rate of bulk PdSO₄ formation, thus causing faster and irreversible deactivation. It is probable, however, that the details of the mechanism are more complex and that water, instead

of favoring SO_2 desorption from the support, induces its further reduction in the presence of methane to H_2S which reacts with Pd to form PdS further converted to bulk-like PdSO_4 species.

The understanding of the details of this mechanism, of the effects of in situ high temperature regeneration, and of the role of the support in changing stability and reducibility of these species (titania, for example, promotes reducibility) are necessary to develop both more resistant catalysts to deactivation or catalysts which can be self-regenerated in situ during high load engine conditions.

3.1.3. Alternative supports

Alumina and zirconia are the most studied supports for palladium, but other types of supports have also been analyzed to improve performances. Interesting results have been obtained in particular for palladium exchanged zeolites (see Section 3.2).

The use of Pd^{2+} exchanged zeolite 13X for methane combustion was first reported by Firth and Holland [68] and Rudcham and Sanders [69]. More recently Pd^{2+} exchanged ZSM-5 zeolites have been reported which show much more interesting properties [14]. For a comparable palladium loading, Pd/ZSM-5 shows comparable activity at temperatures ca. 70–80°C lower than PdO/ Al_2O_3 , but in the latter higher loadings (and thus activity) are possible differently from Pd/ZSM-5. The enhanced specific activity is related to higher dispersion of palladium and higher reducibility of Pd^{2+} [14]. Tests were made at a GHSV of 30,000 h^{-1} , but due to the presence of limits to intraparticle diffusion in the zeolite pore structure it may be expected that the activity will drop for higher space-velocities more drastically than in oxide-supported Pd catalysts.

Li and Armor [14] also observed that different zeolite topologies (ZSM-5 and mordenite) do not lead to different rates of reaction in fresh samples, but large differences in steamed samples. In both zeolites, however, a large irreversible deactivation was observed. Montes de Correa and Luz Villa [70] instead observed that the turnover frequency (TOF) is higher in Pd/ZSM-5 than in Pd/mordenite. They also observed that the TOF significantly drops in over-exchanged samples, indicating that Pd in excess to the exchange limit (around 3–4 wt.%, depending on Si/Al ratio) is either not active or much less active.

By comparison, in Pd/ Al_2O_3 samples the activity was found to increase up to a Pd loading of about 10 wt.%.

Notwithstanding the potential interest in Pd-zeolite catalysts for low temperature methane oxidation, activity on a catalyst weight basis and stability are too low compared to Pd supported on alumina or zirconia. Other zeolite topologies, however, may lead to superior catalysts, and therefore, this area of research offers interesting prospects for the future.

Thermal and hydrothermal stability, morphology and size of the metal particles, and resistance to deactivation may be in principle controlled by direct inclusion of Pd particles in a porous oxide matrix, such as silica. This is the reason for interest in Pd/ SiO_2 catalysts prepared by the sol-gel technique [71,72]. Fierro et al. [71] observed that samples prepared in this way are characterized by Pd particles trapped in silica micropores, while they are located in meso- and macropores using conventional impregnation techniques. The latter situation allows higher activity, as reasonably expected, but Fierro et al. [71] did not investigate the resistance to deactivation which is the main reason to develop such a type of material. However, they observed that the light-off temperature decreases during consecutive runs and the effect is much more enhanced in sol-gel samples than in classical impregnated samples. They attributed the effect to the formation of $\text{Pd}^{\delta+}$ species which promote activity. Encapsulation of Pd particles in the porous silica matrix allows stabilization of such species, and thus considerably promotes activity during consecutive runs. This indicates the potential interest for this kind of materials and the necessity of more extensive studies also using other types of oxide or mixed oxide matrices, such as $\text{TiO}_2\text{-Al}_2\text{O}_3$ or $\text{ZrO}_2\text{-Al}_2\text{O}_3$ for the encapsulation of the Pd particles.

The use of SiC as a high thermal conductivity support for Pd has also been investigated [73]. The activity of these materials was found to be low, but the characteristics of resistance to deactivation are good due to the partial encapsulation of Pd particles in the silica layer formed on the surface of the support. These results clearly evidence the need for further study of these effects to control stability and resistance to poisoning of supported Pd catalysts.

3.2. N₂O

Nitrous oxide is an important greenhouse gas with a long life time of about 150 years in the atmosphere, it has 270 times the greenhouse potential of CO₂ (on a weight basis and when calculated over a 100 years time span), it is broken down in the stratosphere by photolysis and oxidation, and it is also an important source of stratospheric nitrogen oxides which initiate a chain of cyclic reactions leading to stratospheric ozone destruction [61]. The limitation of its emissions has, thus become a significant target in the control of anthropogenic emissions and in particular in the short term from those sources, such as stationary and mobile combustion processes or chemical processes which can be effectively controlled by clean-up methods [74,75]. It is estimated that anthropogenic N₂O emissions in Europe must be reduced from the present value of 1200–1300 kt N₂O–N per year to about 200–250 kt N₂O–N per year in order to reach a climate goal aiming to limit further global warming to 0.1°C per decade.

Achieving this goal requires the development of N₂O abatement technologies which can be applied to the treatment of off-gas from two main types of applications: (i) chemical processes for the production and use of nitric acid; and (ii) fluidized bed waste combustion. Both types of processes are characterized by the presence of N₂O with concentrations below 1% in the presence of other components, such as oxygen, water, NO, etc.

Commercial catalysts and technologies for N₂O decomposition do not show enough activity/stability for the cases cited above. Thus, there is a strong need for efficient and economical technologies which guarantee the elimination of N₂O from the off-gas of combustion and chemical manufacturing processes. Of particular relevance is the activity at low reaction temperatures.

Research on these new catalysts has been primarily focused on Rh-based catalysts [76–79], but recent interesting results have also been reported for Pd-based and Rh-free catalysts [27]. In particular, hydrotalcite-like (HTlc) compounds containing different combinations of bivalent (such as Co or Pd) and trivalent (such as Al, La) cations have been studied. The Pd–La, Al–HTlc compounds (Co/Pd/La/Al) were shown to have high activity (around 60% conversion at 300°C, although in the absence of water and O₂

in the feed). Stable activity in the presence of O₂ and SO₂ requires reaction temperatures higher than 450°C. The XRD data suggested that the presence of the PdO phase is required to have improved activity, while the Mg-spinel phase is necessary to have stable activity in the presence of SO₂.

Although these results are interesting, the performances of other catalysts for N₂O decomposition still remain superior under practical conditions of application. However, such Pd-containing HT catalysts may be interesting as components of catalysts for NO_x reduction in oxidizing conditions in the emissions from lean burn or diesel engines, where N₂O forms in relevant amounts. There are, thus interesting prospects of application of this type for Pd-based catalysts.

4. Palladium exchanged zeolites for conversion of NO by CH₄

Since Pd–H/ZSM-5 was first reported to be effective for reduction of NO by CH₄ in the presence of O₂ [80], several authors have investigated this reaction on the same kind of catalysts [81–87] or other type of supported Pd catalysts, such as PdO/TiO₂ [88,89], PdO/YSZ (yttria-stabilized zirconia) [90] and PdO/Al₂O₃ [16]. The reason for the interest was the possibility to develop an alternative selective catalytic reduction (SCR) process (for stationary sources) to that based on NO_x reduction by ammonia in the presence of O₂ on V–W/TiO₂ based catalysts. The latter, in fact, show some drawbacks, such as the presence of ammonia slip and the formation of some ammonium sulfate/bisulphate on heat exchangers downstream from the SCR reactor. The SCR using hydrocarbons (alkanes, in particular) would avoid these problems and is, thus of potential interest. Methane is available in several SCR plants, and therefore, was assumed to be the preferable reactant, however, without considering process economics. In fact, the temperature limit for SCR technology is around 300–350°C, because otherwise there is the expense of heating the flue gases. Furthermore, high efficiencies in NO selective conversion to N₂ (above 90%) are necessary. NO reduction with CH₄ occurs at reasonable rates at significantly higher reaction temperatures, and low efficiencies (maximum around 60%) in NO conversion with the formation of relevant amounts of NO₂

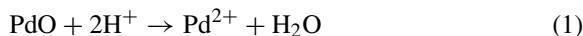
and N_2O as byproducts have been reported. Therefore, the techno-economic prospects for applications of this reaction are not good. The use of propane as a reactant for this reaction using metallo-exchanged zeolite catalysts is preferable in this respect, because due to higher reactivity with respect to methane, high reaction rates at temperatures of 300–350°C with selective NO_x conversion above 80% are possible [91,92]. Also the application of Pd-based catalysts for the reduction of NO_x by CH_4/O_2 in exhaust streams from lean burn NGVs does not appear feasible due to low reaction rates below 300°C. It may be concluded that the large scientific interest on this reaction and type of catalysts is not supported by good prospects for application. Nevertheless, there are scientific motivations for understanding the reaction mechanism and the active state of palladium species during reaction.

4.1. Reaction mechanism and nature of Pd active species

The question of the reaction mechanism of NO reduction in Pd/ZSM-5 samples was early recognized. Nishizaka and Misono [80] indicate that NO reduction proceeds via a first step of NO oxidation to NO_2 . Acid sites of the zeolite are needed for this step. Acid sites also synergistically interact with Pd sites to activate methane. Furthermore, acid sites are needed to maintain disperse Pd ions and this explains why Pd-Na/ZSM-5 is inactive compared to Pd-H/ZSM-5. Kinetic isotope effects confirmed that NO oxidation is the rate determining step [93]. A similar effect of acidity on the palladium activity has been observed by Loughran and Resasco [94] using mixtures of Pd/SiO₂ and H/ZSM-5, $\text{SO}_4^{2-}/\text{ZrO}_2$ and other acidic catalysts. They also concluded that NO oxidation takes place on acidic sites, while acid and Pd sites cooperate in the mechanism of NO_2 reduction by methane. Using EXAFS, the same group also indicate that acidity is needed to maintain Pd in a highly dispersed state (Pd^{2+}), while palladium on non-acidic supports forms PdO clusters [95]. However, the question of the state of Pd during reaction and which species is active in NO reduction is more complex, being present relevant phenomena of in situ changes in Pd species.

Sachtler et al. [83] reported that the exposure of Pd-catalysts to a $\text{NO}_2\text{-CH}_4\text{-O}_2$ mixture induces reconstruction of the active centers of palladium. The

role of acid sites in this effect was explained on the basis of the following equation (protonolysis reaction)



Bell et al. [96] indicated that palladium active species are stabilized at the pair sites of the next-nearest-neighboring Al site of zeolite in the forms of a $\text{Z}^-\text{H}^+(\text{PdOH})^+\text{Z}^-$ species, where Z^- indicates the zeolite framework. More recent results of the same research group [97] showed that the state of Pd in Pd-H/ZSM-5 is a strong function of the reaction conditions. When O_2 is present, the $(\text{PdOH})^+\text{Z}^-$ species does not reduce, independently of the reaction temperature, while in the absence of O_2 fast reduction is observed (above 340°C) with formation of small Pd particles. These Pd species rapidly reoxidize to PdO when O_2 is admitted. Depending on the presence of oxygen and reaction temperature, different palladium species are, thus present. The Pd^{2+} (PdOH^+) species was also found to be about 1–2 orders of magnitude more active than Brønsted acid sites in the reduction of NO by CH_4/O_2 .

Kikuchi et al. [18] also agree that the active species in the reduction of NO by CH_4/O_2 is a hydroxylated Pd species which forms by reaction of H_2O with Pd^{2+} to give a $\text{H}^+[(\text{PdOH})]^+$ species stabilized by next-nearest neighboring Al sites in the zeolite framework. The amount of isolated Pd^{2+} cationic sites was found not to be affected by exposure to $\text{NO}_2\text{-CH}_4$, $\text{NO}_2\text{-CH}_4\text{-O}_2$, or $\text{CH}_4\text{-O}_2$ mixtures at 400°C, while the amount of NO adsorbed was changed after exposure to reactants, due to the generation of H_2O which reacts with Pd^{2+} to form Pd-hydroxyl species. The mechanism proposed for the reaction is outlined in Fig. 5a, although some of the intermediates proposed (such as the $\text{Pd}^{2+}(\text{O}^{2-})(\text{NO})$) are not chemically consistent. Primet et al. [17] instead indicate that Pd hydroxyl entities are mobile and may condense into PdO particles outside the zeolite crystallites with a parallel catalyst deactivation.

Bell et al. [97] proposed a different and more detailed mechanism of reduction of NO by CH_4/O_2 (Fig. 5b). NO adsorbs on $\text{Pd}(\text{OH})^+$ sites forming a nitrosyl species which reacts with CH_4 to produce an adsorbed nitrosylic species (CH_2NO , or its isomer CHNOH) with the release of water. The latter species decomposes to a ciano group (coordinated to metal) and H_2O (which desorbs). The CN group

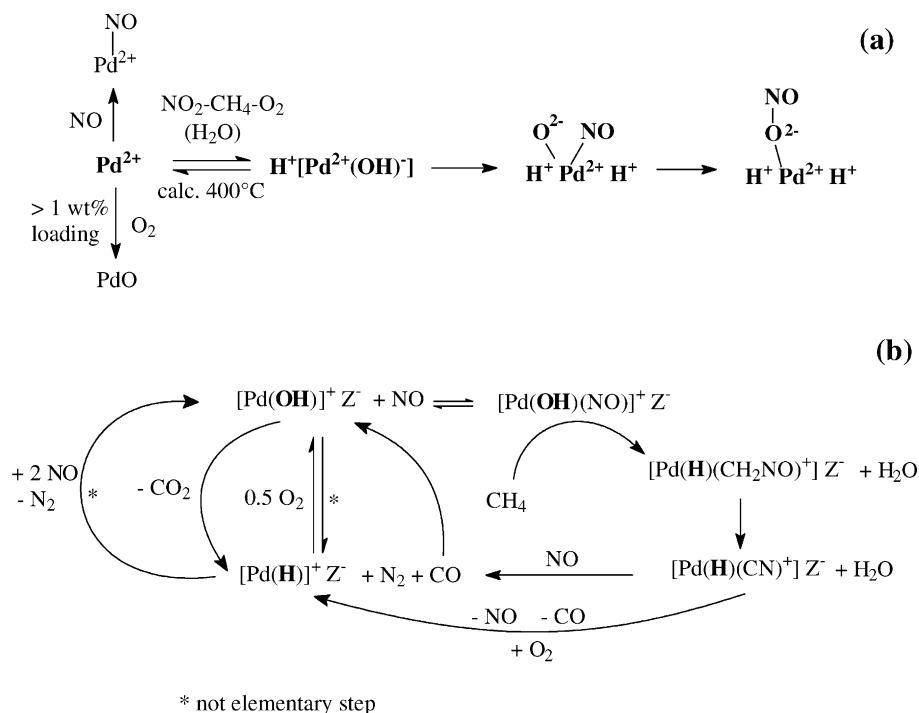


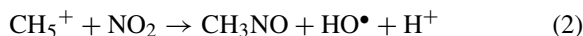
Fig. 5. (a) Mechanism of NO interaction with palladium in Pd–H/ZSM-5 catalysts. Elaborated from Kikuchi et al. [18]. (b) Mechanism for NO reduction by CH₄ over Pd–H/ZSM-5 in the presence of O₂. Elaborated from Bell et al. [97].

can react with either NO or O₂ to form N₂ + CO or NO + CO, respectively. The CN may also react with NO₂ (not indicated in the scheme reported in Fig. 5b) to give N₂ and CO₂. The CO may further react with Pd(OH)⁺ species to give CO₂ and Pd(H)⁺. The latter species may undergo autoreduction with formation of Pd atoms which agglomerate into Pd particles or in the presence of O₂ may reform Pd(OH)⁺ species (rate of reaction is faster with O₂ than with NO).

The NO reduction may also occur on Pd metal particles by the classical NO dissociation mechanism, but when O₂ is present the rate of oxidation of Pd to PdO is faster than the rate of NO dissociation. The PdO is effective in direct methane oxidation, and thus the formation of PdO leads to a net effective decrease in methane available for NO reduction. Nitrito [Pd(OH)(ONO)]⁺ Z⁻ species and positively charged nitrosyl species (NO⁺) were also detected, but their role in the reaction mechanism was neglected.

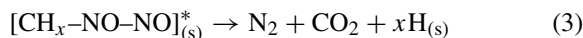
Although not all steps of this reaction mechanism are fully demonstrated, this proposed reaction mechanism [97] reasonably interprets the reactivity data,

apart from the role of NO₂ pointed out by several authors. To explain this role, Adelman and Sachtler [83] suggested the following equation:



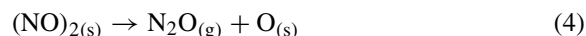
However, the methane protonation by superacid zeolite sites is not a likely reaction.

On Pd/TiO₂ catalysts, Kumthekar and Ozkan [88,89] suggested instead a different mechanism for NO reduction by CH₄/O₂. Using transient analysis methods with isotopic labeling, they found that NO and CH₄ strongly adsorb/interact with both reduced and oxidized palladium. They suggest that methane is activated on metallic Pd by heterolytic dissociation. The CH_x species reacts with NO to form a methyl-dinitrosyl type surface intermediate which readily decomposes to N₂ and CO₂



The reaction of N₂O formation was instead suggested to take place without a direct involvement of methane,

but by coupling of two NO molecules through a dimeric intermediate



The formation of the dinitrosyl surface species was also suggested to be inhibited by the presence of CH_x (produced by methane dissociation). A role of the NO_2 species in the reaction mechanism was instead excluded. It was suggested that PdO only plays a role in methane combustion. As a result of the different exothermicity of the reactions of NO reduction by CH_4/O_2 and methane oxidation (occurring respectively on Pd and PdO), cyclic phase transformation of palladium on the surface occurs and self-sustained regular oscillations in NO conversion were observed at specific temperatures and oxygen concentrations [98].

In Pd/YSZ catalysts, Lambert et al. [90] observed that methane and NO competitively adsorb on the Pd surface and that O adatoms inhibit dissociative chemisorption of methane. Furthermore, they observed that due to strong chemisorption of NO relative to methane, the reaction tends to be self-poisoning by NO and its dissociation products. An increase in the NO chemisorption strength by doping with Na induces a lowering of both selectivity to N_2 and activity.

Burch and Ramli [16] in alumina-supported Pd catalysts report a relevant formation of NH_3 in the reduction of NO by methane (selectivity about 20%), indicating a mechanism of combination of N_{ads} (produced by NO dissociative chemisorption) and H_{ads} (produced by methane dissociation). Oxygen would inhibit NH_3 formation by inhibiting the formation of H_{ads} , but a higher Pd coverage with oxygen would prevent NO dissociation. In Pd-Co-H/ZSM-5 catalysts, Kikuchi et al. [99] instead pointed out that the role of cobalt (which increases catalyst activity in NO reduction by CH_4/O_2 as well as hydrothermal stability) is twofold: it promotes NO oxidation to NO_2 (indicated as the rate determining step for the reaction) and dispersion of palladium ions. Dispersed Pd^{2+} species were also reported by Ohtsuka and Tabata [100] for the reaction. These authors studied the effect of the Si/Al ratio on the activity and durability of Pd-ZSM-5 catalysts.

While a different behavior may be expected in the reaction mechanism of NO reduction by CH_4/O_2 , depending on the type of support, it is also evident from the above discussion that the differences in the reaction

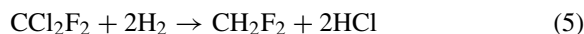
mechanism are too large to be explained by the relatively small differences in the catalytic behavior between the different samples. It is also evident that NO may induce some modification in the surface reactivity and can induce some redispersion of Pd (as discussed above), but it is difficult to suppose a complete change in the reactivity. The proposed reaction mechanisms and nature of the Pd species present are not consistent with those hypothesized for the low temperature oxidation of methane (see Section 4).

In conclusion, several advances have been made to understand the mechanism of NO reduction by CH_4/O_2 on Pd-based catalysts, but quite contrasting hypotheses are presented in the literature which do not allow a unifying view of the reaction mechanism. Although practical interest may be limited, understanding this chemistry is worthwhile for the possibility of being able to develop catalysts able to selectively activate an inert hydrocarbon, such as methane and use it as a selective reductant for NO in the presence of large quantities of oxygen. This fascinating chemistry would probably established the basis for developing a new type of selective hydrocarbon conversion over this kind of material, especially Pd-zeolite catalysts.

5. Conversion of halogenated hydrocarbons

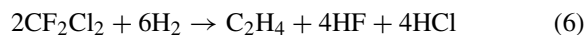
The Montreal protocol on substances that deplete the ozone layer banned the use of chlorofluorocarbons (CFCs), but they are still widely used (mainly as a refrigerant and foam blowing agent) and it is of utmost importance to prevent the banked CFCs from being emitted into the atmosphere. A useful technique is to convert them, using catalytic hydrodechlorination processes to hydrofluorocarbons (HFCs) by substituting one or more halogen atoms with H [101]. In fact, the C-H bond is more labile than C-Cl bond, and thus the life time of the pollutant in the troposphere is much shorter, and thus its effect on ozone layer. At the same time, the physico-chemical properties of the compound does not change too much (for example, for its application in refrigerators).

An example is the conversion of CCl_2F_2 (CFC-12) into CH_2F_2 (HFC-32) [19,20,102–105]



Other CFCs studied in catalytic hydrodechlorination reactions include $\text{CF}_3\text{CCl}_2\text{F}$ [106,107] and $\text{CCl}_2\text{FCClF}_2$ [108]. The Pd-based catalysts supported on different types of supports (alumina, titania, zirconia, AlF_3 and carbon) are the preferable type of materials used for this application, due to good activity (in carbon–halogen hydrogenolysis) and acceptable stability. Both these properties depend considerably, however, on the type of support and CFC reactant.

In the case of CFC-12, a selectivity over 80% in HFC-32 may be obtained, and therefore, the conversion for recycle is economical. For some CFCs, however, the selectivity in the conversion to reusable HFC is not enough to justify a process and, on the other hand, their disposal requires special procedures, their being classified as hazardous materials. A possibility reported in the literature is the catalytic complete dehalogenation in order to form hydrocarbons which can be recycled or safely burn out. An example is the conversion of C1 CFCs into dechlorinated C2 products which may be used as monomers (C_2H_4 and C_2F_4) for industrial processes of polymerization [109]



Pd catalysts show a selectivity up to 75% in C2 + C3 completely dehalogenated hydrocarbons (C_2H_4 , C_2H_6 , C3), but a mixture of products is obtained which is not suitable for chemical applications. The Pd shows nearly zero selectivity to the most interesting product (C_2F_4), but also on other noble metals, selectivity is not higher than 4% [109]. This method is, thus attractive, but not useful with the present type of catalysts. The method, however, may be interesting for converting halogenated chemicals [110–112] used, for example, as cleaning solvents, such as 1,2-dichloroethane



High selectivities are possible using Pd–Ag/ SiO_2 bimetallic catalysts [111,112]. The process may be interesting when relatively large amounts of these chlorocarbons must be treated, but their recovery is not possible. Other more relevant cases of application include chlorinated waste recycling or inertization in refinery, petrochemical and energy applications and include relevant industrial problems, such as safe disposal of polychlorobiphenyls and chlorinated alkanes [113].

When low concentrations are present in the emissions, the preferable solution is their deep oxidation [21,114–118]. A specific relevant problem in these cases is to have a high efficiency at low reaction temperature (below 500°C), in order to avoid the possibility of aromatization reactions with formation even at the sub-ppm level of very harmful products, such as PCB and dioxins. The Pd-based catalysts are used for this reason.

Halogenated VOC emissions are associated with a wide range of industrial processes. For instance, large amounts of 1,2-dichloroethane are emitted from vinyl chloride production plants and trichloroethylene is a widely used solvent in metal degreasing processes. Another relevant case regards the elimination of halocarbons from the stripping air used to decontaminate groundwater and soil.

There are different problems of selectivity and activity in the three types of applications discussed above. Due to the presence of oxygen in the total oxidation case, while of H_2 in dehalogenation reactions, the state of active palladium species should be different. Even so, there also are common aspects: the problem of activating the C–halogen bond, the possibility of formation of C–C bonds in the adsorbed intermediate and in general the mechanism of surface transformation and reaction intermediates, the in situ modification of the support by the halogen atoms and the presence of more or less fast deactivation processes. The following discussion is focused on the above questions.

5.1. Hydrodechlorination and dehalogenation

The conversion of CCl_2F_2 to CH_2F_2 is the most discussed case. Palladium on activated carbon is a very suitable and stable catalyst for this reaction [104,107]. Performance data indicate that using a high H_2 to CCl_2F_2 ratio (in the 6–20 range), the activity can be maintained over 80% with a selectivity to CH_2F_2 of over 80% for 1600 h^{-1} of time on stream (reaction temperature about 230°C). The reaction network for the reaction is based on a sequence of in series reactions (Fig. 6), the relative rate of which depend considerably on the H_2 to CCl_2F_2 ratio. A higher concentration of hydrogen on the surface favors the adsorption steps requiring more hydrogen, although a constant selectivity with respect to methane formation was instead observed [119]. The Pd, with respect

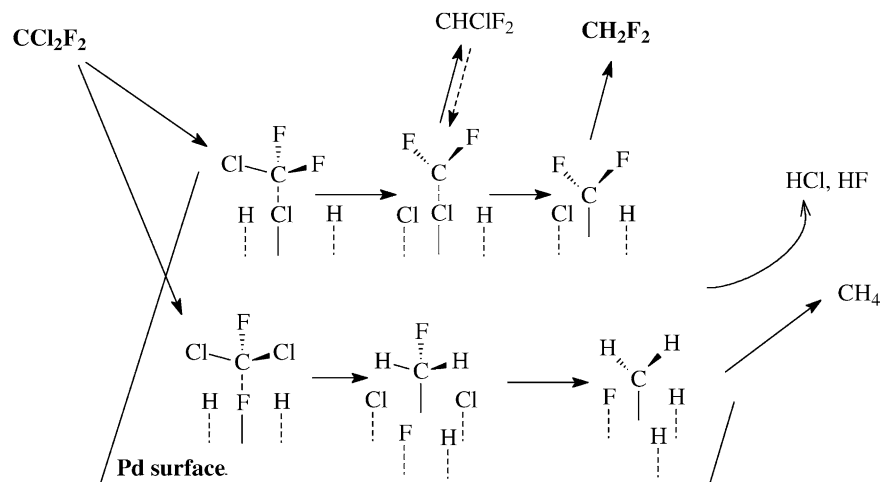


Fig. 6. Mechanism of CCl_2F_2 hydrogenolysis over palladium. Elaborated from Wiersma and coworkers [102,103].

to other noble metals, shows a lower selectivity to CHClF_2 and higher selectivity to CH_2F_2 [107]. The different noble metals do not show relevant differences in the chemisorption of CCl_2F_2 or the relative products of hydrogenolysis. However, they show differences in the presence of carbon and halogen atoms after the reaction. Characterization of palladium catalysts after hydrogenolysis of CCl_2F_2 indicated the formation of a $\text{PdC}_{0.15}$ phase and a surface coverage by chlorine atoms of about 0.3, while a much lower amount of fluorine atoms was detected [107,120].

A key surface intermediate in the reaction mechanism was suggested from Coq et al. [105] and later from Moulijn et al. [102,103] to be a fluorinated carbene-type species (CF_2) (Fig. 6). The selectivity to CHClF_2 and CH_2F_2 is determined by the amount of chlorine present on the catalyst surface and the ease of chlorine removal from the catalyst surface by means of hydrogen. Palladium shows the lower temperature for removal of chlorine and as a consequence the higher selectivity for CH_2F_2 .

This property also explains why palladium is widely used as the active component in catalyst formulations for chlorocarbon conversion. Another relevant characteristic of palladium is that its reactivity is very low in the chlorine/fluorine exchange, and thus low amounts of CHF_3 are formed, for example. This halogen exchange reaction is the only one which occurs in the absence of H_2 [20] and may be an indicator of the

competition between surface coverage by hydrogen and by CFCs.

The hydrogenolysis of the C-Cl bond is faster with respect to that of the C-F bond, and this explains why selectivity to $\text{CHClF}_2 + \text{CH}_2\text{F}_2$ is over 90–95%. However, if adsorption of CCl_2F_2 occurs via fluorine coordination, C-F and C-Cl hydrogenolysis can occur at the same time and a carbene-intermediate forms which leads to the final formation of methane. This pathway is of minor importance, but may explain why the methane selectivity is independent of the H_2 to CCl_2F_2 ratio in the feed and catalyst deactivation. Data of Karpinski et al. [19] who compared CH_2Cl_2 and CCl_2F_2 behavior were in agreement with the indication that methane forms by hydrogenation of a surface carbene intermediate.

Although the use of a high H_2 to CCl_2F_2 ratio in the feed limits deactivation, the catalyst activity progressively decreases with time-on-stream [102,103]. The following modifications in the catalyst were observed in the Pd on carbon catalyst after CCl_2F_2 hydrogenolysis: (i) formation of a palladium carbide phase and coke deposition; (ii) redispersion of noble metal caused by chlorine atoms or compounds; and (iii) sintering of the metal, the latter when a high H_2 concentrations in the feed is present. The rate of deactivation was, thus found to have a minimum for a H_2 to CCl_2F_2 ratio in 6–10 range. For lower ratios the main cause of deactivation was associated with

coke deposition, while for higher ratios with sintering of palladium [102,103].

The question of the relationship between metal dispersion and catalytic behavior, however, deserves more study, because other studies on alumina supported Pd catalysts showed that poorly dispersed Pd catalysts have a higher TOF [19,121], while Baiker et al. [20] found no correlation.

Baiker et al. [20] also reported the formation of AlF_3 in $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts during use in CCl_2F_2 hydrogenolysis, in agreement with earlier results [105,122–124]. However, the previous investigation [105,122–124] suggested that the fluorinated alumina phase promotes the behavior and selectivity of palladium, because electron-deficient Pd species are generated. Baiker et al. [20] instead suggested that the AlF_3 phase is responsible only for promotion of the Cl/F exchange reaction, causing a lowering of the selectivity. The selective CH_2F_2 formation from CCl_2F_2 was attributed by Baiker et al. [20] to a Pd(C) phase formed by incorporation of carbon into the Pd lattice. Interstitial carbon was also claimed to be responsible for methane formation.

The possibility of further promotion of the catalytic behavior of supported Pd catalysts by doping has also been studied (although not very systematically) as claimed in patents [125]. The problem is especially relevant for CFCs other than CCl_2F_2 for which already good behavior has been shown by unpromoted Pd catalysts. The Pd has been doped with K, Fe, Co, Ag [126], Al, Ti and Zr [124] and Bi, Tl [127,128], but the results have not been particularly relevant. More recently, the possibility of modification of Pd by forming a bimetallic compound with Re was also explored [129]. However, Re only depresses activity and promotes deactivation.

More interesting results have been obtained by adding ZnO to a $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst for the hydrogenolysis of 1,1,2-trichlorotrifluoroethane. Using a Pd:Zn ratio of 1:2, selectivities over 85% to CH_3CF_3 at around 10% conversion are possible. The addition of zinc results in increased dispersion of palladium metal particles and stabilization of palladium against the formation of bulk palladium chloride or fluoride leading to catalyst deactivation. Probably, a Pd–Zn alloy forms on which the equilibrium coverage of the adsorbed chlorofluorocarbon and halohydrocarbon species is favorably modified [130].

A Pd–Ag alloy was instead found to promote the selective conversion of chlorinated alkanes (1,2-dichloroethane) to alkenes (ethene) [111,112,131]. It is suggested, however, that the active sites are silver atoms present at the surface of the Pd–Ag alloy particles. Silver is more active than Pd in C–Cl bond dissociation, but Cl does not desorb from silver. The Pd promotes H_2 dissociation and migration of H atoms to silver by spillover, and thus regeneration of chlorinated silver. However, Pd also promotes hydrogenation of ethene to ethane which decreases selectivity to the alkene. It is also suggested that chlorine atoms induce positively charged surface silver atoms ($\text{Ag}^{\delta+}$) which are the effective active sites.

A question in halocarbon conversion on Pd catalysts is whether or not the reaction is structure-sensitive, because different results have been reported in the literature regarding this question, as mentioned before. Buelow et al. [132] have studied the transition state for metal-catalyzed dehalogenation on the Pd(111) surface using the method of the substituent effect. The results indicate that the transition state for dehalogenation (breaking of C–X bond, where X is a halogen atom) is homolytic and occurs early in the reaction coordinate. The implication for catalytic hydrodehalogenation is that the transition state is much like the initial adsorption state and that the nature of the catalytic surface does not affect the energy of C–X bond dissociation step, because the energy of the adsorbed reactant and transition state would be similarly influenced from the substrate. This implies that the reaction is structure insensitive. On the other hand, Somorjai et al. [133] studied the reaction of CCl_2F_2 hydrodechlorination on Pd(111) and Pd(110) single crystals as well as polycrystalline palladium foils. The latter were observed to be more active than single crystals, while Pd(111) and Pd(110) single crystals showed minor differences in the TOF, selectivity and rate of deactivation. The difference was interpreted in terms of a higher amount of steps and kinks in polycrystalline Pd, but they also found that the chlorine surface concentration was important in determining the catalytic behavior. It is, thus probable that the difference between single crystals and polycrystalline Pd should also be related to a different capacity to accommodate surface chlorine atoms in the two cases.

It may be concluded that the hydrodehalogenation reaction is not a structure-sensitive reaction, and the

differences in the catalytic behavior as a function of the Pd particle size, for example, found by some authors should be instead related to other properties changed at the same time.

5.2. Oxidative destruction

Generally, two kinds of catalysts are used in the oxidative destruction of halocarbons: noble metals supported on oxides and metal oxides (Cr/alumina, LaMnO₃ perovskite, etc.) or metal-containing zeolites (Cr/ZSM-5, etc.). Noble metals based catalysts are the most active (a relevant aspect, as discussed previously). With respect to the case of hydrodehalogenation, the support of palladium (alumina mainly) plays a relevant role in the reaction mechanism, being active itself in the reaction as discussed below.

In all systems, catalyst deactivation by poisoning by chloride ions, sintering and formation of volatile metal oxychloride is an important problem. The Pd shows a reduced sensitivity to these aspects and for this reason its use in this reaction is worthwhile, notwithstanding limited literature data on the behavior of Pd-based catalysts in the oxidative destruction of halocarbons.

Gonzalez-Velasco et al. [21] have investigated the complete catalytic combustion of 1,2-dichloroethane (DCE) and trichloroethylene (TCE) over alumina supported noble metals (Pd and Pt). Palladium catalysts were found to be more active than platinum catalysts in the oxidation of both DCE and TCE. The first is completely converted at temperatures below 400°C, whereas TCE requires temperatures higher than 550°C, reasonably due to stronger chemisorption on the metal. The palladium catalyst shows light-off temperatures around 20–40°C lower than platinum, but with Pt the formation of CO is significantly lower. Alumina without noble metals was found to be active in the same range of temperature and partially contributes to overall activity.

Both CO_x and HCl were the main products of reaction at the temperature of complete conversion, but some products of incomplete combustion and Cl₂ formation were also detected. The latter originate from the Deacon reaction [134]. The Pd forms higher amounts of Cl₂ with respect to Pt and this is a drawback of the reaction, being Cl₂ removal more difficult. In addition, Cl₂ promotes the possible formation of traces of chlorinated aromatic compounds at high

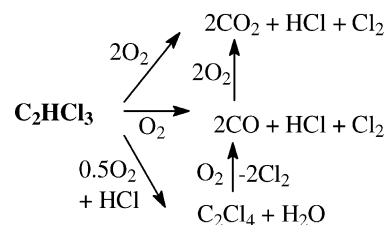


Fig. 7. Reaction network in trichloroethylene oxidative conversion on Pd/Al₂O₃. Elaborated from Gonzalez-Velasco et al. [21].

reaction temperatures. At reaction temperatures lower than complete conversion, relevant formation of product intermediates was also observed, such as C₂Cl₄ in TCE oxidation. The proposed reaction network is reported in Fig. 7.

Gonzalez-Velasco et al. [21] also noted that the chlorine balance was within only 70–80% of theoretical and relevant chlorine retention from the catalyst was observed. This indicates possible catalyst deactivation, although data have been not reported on this aspect.

A problem in halocarbon conversion, especially relevant when complex mixtures, such as those deriving from groundwater stripping emissions, is how to predict the global behavior when various halocarbons or VOCs are present in the feed. In fact, the behavior in the conversion of these chemicals on supported noble metals considerably depends on the strength of their adsorption and on the presence of halogen atoms (released during the reaction) on the catalyst (see discussion in Section 5.1). Therefore, significant interferences in the light-off curves of the single halocarbons can be expected, when a mixture is used.

This problem was addressed by Gonzalez-Velasco et al. [118], but other data on this question are very limited. They found that the addition of non-chlorinated hydrocarbons (hexane and toluene) to a multicomponent chlorinated feed (DCE, TCE, dichloromethane, DCM, and 1,1-dichloroethylene, DIC) determines a change in the oxidizability order of the chlorocarbons. DIC and TCE oxidation was promoted, while DCE oxidation was inhibited. Probably, the oxidation of non-chlorinated hydrocarbons (which adsorb stronger on the catalyst than, for example DCE) would have two effects: (i) block some sites of adsorption of halocarbons; and (ii) maintain the catalyst in a more reduced state, thus changing the catalyst reactivity. It

is also possible that the adsorption of non-chlorinated hydrocarbons modifies the surface work function of palladium (thus, changing its adsorption properties) and that the combustion of these hydrocarbons enhances local catalyst heating and reactivity. The latter indication is supported by the general observation that chlorocarbons experience faster ignition when non-chlorinated hydrocarbons are also fed. The behavior of complex mixtures in the complete conversion on supported noble metals is, thus far from being understood, although this problem must be addressed to apply deep catalytic oxidation to treat stripping emissions.

Another component usually present in real feeds, but the effect of which has not often been considered, is water. Nieuwenhuys et al. [117] reported that in the presence of water in the oxidation of TCE on Pd/Al₂O₃, the conversion does not change relevantly, but the formation of tetrachloroethylene is significantly depressed and C-balance improves. Water competes for adsorption, promotes HCl desorption, promotes hydroxyl formation which influences surface reactivity (see below) and may dissociate to generate H₂ in some conditions. Also in this case, various effects are, thus possible which cannot be simply predicted.

The details of the reaction mechanism of catalytic oxidation of halocarbons have been studied by various authors mainly by FTIR spectroscopy, although mainly using alumina or mixed oxide catalysts [117] and references therein. More limited information is available on supported Pd catalysts, but it should be considered that probably the catalyst must be considered bifunctional, i.e. both palladium and the support participate in the reaction mechanism. The suggested reaction mechanism for DCE oxidation is outlined in Fig. 8.

Even at room temperature, DCE readily converts to vinylchloride, either by double C–Cl breaking on Pd or by the action of Lewis acid sites of the support. In the case of Pd/Al₂O₃, the chlorination of alumina would produce AlCl₃ like species which are known to be quite active in the dehydrochlorination of DCE. The reaction on alumina is very dependent on the degree of dehydroxylation of the alumina surface [135]. The vinylchloride intermediate can be protonated by surface Brønsted sites to form a carbonium ion which may be attacked by nucleophilic oxygen species to form an alkoxychlorine species which decomposes to form acetaldehyde, leaving chloride ions on the surface. Acetaldehyde may be oxidized to form surface acetate species relatively resistant against further oxidation

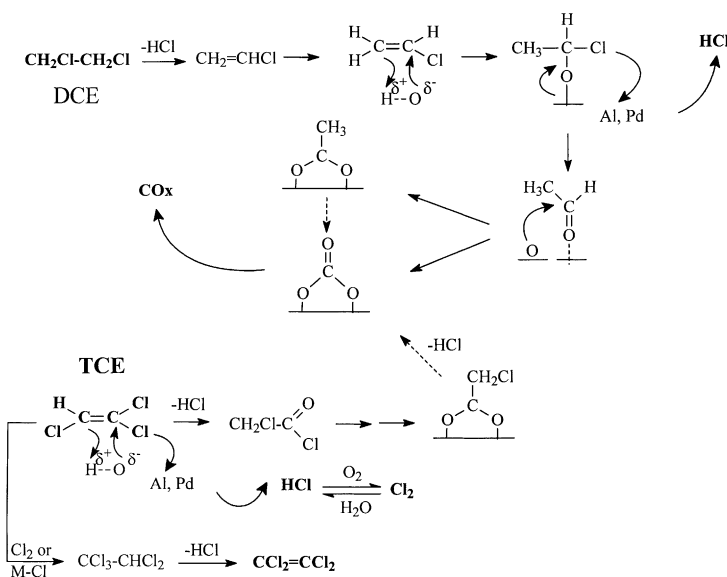


Fig. 8. Reaction network in DCE and TCE oxidative conversion on Pd/Al₂O₃. Elaborated from Feijen-Jeurissen et al. [117].

and carboxylate species. In the case of TCE oxidation, an intermediate similar to vinylchloride forms by adsorption, but contains two more chloride atoms. Its conversion, thus generates a monochloroacetylchloride surface species which has a faster hydrolysis rate to CO and dichloromethane. The formation of tetrachloroethylene derives instead from the addition of Cl₂ to TCE followed by dehydrochlorination (Fig. 8). The Cl₂ is generated by the equilibrium oxidation reaction of HCl (Deacon reaction).

6. Conversion of VOCs or other components of gaseous emissions

Volatile organic compounds (VOCs) give a major contribution to air pollution, either directly through their toxic or malodorous nature, or indirectly as ozone and smog precursors. The VOC emissions result primarily from transportation activities (light cars and trucks — around 40% of total VOC emissions), stationary sources, solvent emissions, industrial manufacturing and fuel combustion. A recently recognized problem also regards the indoor concentration of VOCs (i.e. inside buildings and homes) which often is above the allowed limits. Conversion of VOCs both on supported noble metals and mixed oxides (supported or not) have been studied in detail. The majority of commercial catalysts belong to the first category and consist of Pt or Pd or both, supported usually on a γ -Al₂O₃ carrier. There are several open questions regarding Pd-based catalysts. The more relevant are related to the following aspects:

- Understanding the behavior of complex reaction mixtures [1] and the mutual influence of VOC's on the surface adsorption–desorption processes and light-off curves [5].
- Role of surface contamination (by chloride and water, for example [136]) on reactivity.
- Relationship between palladium oxidation state and activity towards different VOCs and CO [137,138].
- Inhibition effect of CO on the oxidation of VOCs [139].
- Possibility of promoting catalytic behavior by incorporating the noble metal into a zeolite framework [140,141] (a further advantage is the possibility to have a combined sorption–catalyst system for

applications in which the catalyst operates cyclically as sorbent and as combustion catalyst [142]).

However, the presence of a large number of commercial applications using these catalysts clearly shows that the key properties are known. Attention in this section, thus is focused on other types of less studied applications which may open new prospects for applications as well as provide evidence for the polyfunctional characteristics of Pd as the active component of catalysts for the treatment of gaseous emissions.

An interesting example of a less conventional application of Pd-based catalysts is for the low temperature removal of ethene from fruit storage areas [22]. Ethene is a gaseous plant hormone that causes fruit ripening. Removal to less than 0.03 ppm is important to preserve fruit in an unripened state. Furthermore, the catalyst must operate with reduced oxygen concentrations and in the presence of water (a controlled atmosphere is usually utilized to maintain fruit; a typical composition is 2% O₂, 5% CO₂ and 100% humidity at 0°C). The catalyst must, thus operate up to ppb removal levels, and at a reaction temperature as close as possible to room temperature, to minimize heating of the storage area. This would also make the catalytic device less expensive and make it easier to install in transportation containers and shop storage areas.

It is evident that very severe constraints exist on the development of this catalytic device, which however, may also find application in other cases. For example, for VOC removal (formaldehyde, in particular) from indoor air in buildings and homes. Noble metal containing ZSM-5 catalysts, further modified by alkali ions (Cs, Na) and transition metals (Cu²⁺) show good behavior for ethene removal at reaction temperatures below 100°C and stable operations for relatively long times (no loss of activity at 60°C for over 5 g of ethene converted per gram of catalyst [22]).

These catalysts, thus represent a new promising area of application of catalysis to a non-conventional area. Their use in indoor air purification is also envisaged. Another area of interest is in the catalytic combustion of odors in domestic spaces for which ion-exchanged zeolites have been shown to have superior performances [28]. Trimethylamine and other amines are typical odors in domestic spaces and palladium has a

higher activity than other active components in the conversion of N-containing VOCs. A specific problem encountered in developing catalysts for this application is the necessity to avoid NO_x formation in the combustion process. Bicomponent metal-containing zeolites (for example, Pd and Cu or Fe) would, therefore, probably be necessary, similarly to the previously discussed case.

Pd-based zeolites, further modified by alkali ions to tune acidity and by transition metal ions (Cu^{2+} and Fe^{3+} , for example) to improve catalytic behavior, are thus a new type of catalyst which may find application in the wide and commercially relevant area of the low temperature removal of VOCs.

A different interesting case of pollution removal at low temperature in which Pd-based catalysts may play a relevant role is that of removal of ozone and other gaseous pollutants from ambient air using catalysts coated on vehicle radiators [23,143]. The temperature of radiators typically ranges from 25 to 100°C, and thus the catalyst must be active in this range of temperatures. The radiator was first coated by a washcoat and the noble metal was deposited on it. Both Pd and Pt show a high activity in the conversion of ozone in this range of temperatures, but only Pd is not deactivated in the presence of water vapor. Partial removal of hydrocarbons, CO and NO also occurs at the same time [143].

The reduced sensitivity of Pd to inhibition by water as compared to Pt, for example, is a characteristic which finds application for another relevant case, the selective oxidation of ammonia to N_2 in wet streams [26]. There are several cases of wet streams containing ammonia which should be catalytically treated before being sent to vent or to other purification methods (flame or catalytic combustion, for example, where NH_3 may give rise to NO_x formation above lawful limits). These include ammonia removal from stripping air in petrochemical processes or soil/water decontamination, air purification in sewage disposal areas, and treatment of effluents in anaerobic sludge digestion or wet oxidation. The Pd/ZSM-5 shows the best combination of characteristics of selectivity to N_2 , reduced sensitivity to inhibition by water and activity at low temperature [26] in comparison with classical catalysts for NO_x selective catalytic reduction by ammonia ($\text{V}_2\text{O}_5/\text{TiO}_2$), other noble metals (Pt, Rh) supported or ion-exchanged in zeolites, and

other transition metal containing zeolites, such as Co/ZSM-5.

Another relevant case regards the elimination of ammonia from gasified biomass (biogas) [144]. Biogas is an interesting alternative energy source which would reduce the net CO_2 emissions in the atmosphere. Biogas has a complex composition which depends on several variables, but generally contains around 15% CO, 10% H_2 , 5% methane and light hydrocarbons, 10% H_2O and 15% CO_2 (the remainder is N_2), plus not negligible amounts of ammonia (typically in the 500–4000 ppm range) and NO_x derived from biogenic organo-nitrogen compounds. The presence of the latter two components gives rise to large amounts of NO_x during the combustion of biogas, which must be removed. The direct selective catalytic reduction (SCR) of NO_x by ammonia requires the addition of oxygen, but CO and H_2 oxidation would compete with this reaction and furthermore the NH_3/NO_x ratio in biogas is usually higher than the value for SCR. The alternative, therefore, is to carry out direct low temperature selective oxidation of ammonia using Pd/ Al_2O_3 catalysts [144]. The Pd-based supported catalysts also find application in the catalytic combustion of biogas [24].

7. Conclusions

Palladium, due to its high reactivity in methane and other VOCs, specific characteristics of the reversible PdO/Pd transition, low sensitivity to inhibition by chloride ions and water, good thermal/hydrothermal stability and low volatility of hydroxide or oxychloride species, finds use in a large variety of environmental applications which range from high temperature methane combustion for gas turbines to the removal of low temperature methane and other VOCs and from hydrodehalogenation to oxidative total combustion of halocarbons.

Palladium shows superior performances to other noble metals or mixed oxides in these applications, either supported on oxide carriers or added by ion-exchange to zeolites. Further promotion by alkali or transition metals ions, or by forming alloys with other metals is sometimes useful.

The behavior of Pd-based catalysts in these applications has been discussed here, with specific reference to the reaction mechanisms, structure-activity

relationships, stability of the catalyst and possible inhibition effects. These, indeed, are the key parameters for improving catalyst design and developing both new catalysts and new types of applications.

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