

Sulphur poisoning of palladium catalysts used for methane combustion: Effect of the support

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Abstract

Four different supported palladium catalysts (using alumina, silica, zirconia and titania as supports), prepared by incipient wetness impregnation, were tested as catalysts for methane oxidation in presence of sulphur dioxide. The catalyst supported on zirconia showed the best performance, whereas the silica-supported one showed the fastest deactivation. Temperature-programmed desorption experiments of the poisoned catalysts suggest that SO₂ adsorption capacity of the support plays a key role in the catalyst poisoning.

In order to study the effect of promoters, expected to improve the thermal stability and thioresistance of the catalyst, commercial zirconia modified by yttrium and lanthane was tested as supports. It was found that the presence of these promoters does not improve the performance of the zirconia-supported catalyst.

A deactivation model – considering two different active sites (fresh and poisoning), pseudo-first order dependence on methane concentration and poisoning rate depending on sulphur concentration and fraction of non-poisoned palladium – was used for modelling the deactivation behaviour.

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1. Introduction

Methane is present in gaseous emissions from many processes, such as petroleum processing, carbochemical and petrochemical plants, coal mines venting, farms and biological processes used for solid wastes and wastewater treatment, off-gases of natural gas-powered engines, etc. In the last years methane emissions are of great environmental concern because of its implication in the greenhouse effect [1]. Thermal incineration (the conventional technique) operates at very high temperatures (up to 1000 °C), requiring high-energy consumption and producing noxious by-products such as NO_x. Catalytic combustion is considered as an interesting alternative for the abatement of methane in diluted emissions. The main advantage of this technique is the lower temperature needed, saving energy and reducing the risk of formation of NO_x [2]. Furthermore, the autothermal combustion of dilute methane–air mixtures can be achieved in regenerative reactors (such as reverse flow reactors

or simulated moving bed reactor) at methane concentration so low as 2000 ppm [3,4].

Although this technique is widely developed for the abatement of many volatile organic compounds (VOCs) (aromatic, oxygenated or paraffinic of medium molecular weight), its application to methane is more difficult, since methane is among the hydrocarbons most difficult to be oxidised, requiring higher temperatures than most of the other VOCs.

Most experimental studies on catalytic oxidation have been carried out for more reactive VOCs, at conditions in which the thermal stability of the support is not so important as in the case of methane. It is known that supported palladium catalysts are the most active for methane deep oxidation [5, and references cited therein], and there are many studies focused on the alumina-supported ones. However, alumina is not stable at the temperatures commonly used for methane oxidation (in the range 400–500 °C), as sintering phenomena are favoured at high-reaction temperatures [5,6]. In previous works it has been observed that, at these conditions, zirconia-supported catalysts present better performance than other supports [7].

Another problem often found in methane-containing emissions is the presence of sulphur compounds, which can act

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as catalyst poisons. For instance, hydrogen sulphide, sulphur dioxide or mercaptanes can be present in emissions from carbochemical or biological plants [8]. The adsorption of sulphur compounds on the catalyst active phase can inhibit, partially or completely, the adsorption or the dissociation of the organic molecules and the surface reaction among adsorbed molecules, or modify the electronic and structural surface properties, and hence affect the catalytic properties [6]. Many authors attribute this effect to the strong adsorption of SO_2 and SO_3 (generated by catalytic oxidation of the SO_2 , H_2S or organic sulphur compounds) on the active phase surface [9,10]. In many cases even the formation of palladium sulphates and/or sulphites is reported [11–13]. The catalyst support also seems to play a key role on the sulphur poisoning. So, Hoyos et al. [12] found that SiO_2 -supported catalysts are poisoned faster than alumina-supported catalysts. However, studies on the effect of sulphur compounds in the behaviour of zirconia-supported catalysts are rather scarce, in spite of the great practical interest of these materials for methane catalytic combustion.

Metal oxide catalysts (single/complex oxides, massive or supported) are considered to work better in presence of sulphur compounds [14,15]. However, these materials are less active than palladium catalysts, requiring higher temperatures and requiring higher methane concentrations for working autothermally [4].

For this reason, the development of palladium-based sulphur-resistant total combustion catalysts would be very interesting from an environmental point of view. It must be considered that, even in the case of installation of sulphur trapping devices before the combustor, small amounts of sulphur compounds can be slipped into the reactor. Thus, the development of a mechanistic model for predicting the deactivation of these catalysts is also of great practical interest.

The aim of this work is to study the performance of palladium on different supports as catalysts for the combustion of methane in presence of sulphur compounds, in order to explore the feasibility of the catalysts for the abatement of methane from gaseous emissions containing these compounds. SO_2 was selected as model sulphur compound by two different reasons: it is present in many emissions (carbochemical and petrochemical plants, combustions) and all the other sulphur pollutants (H_2S , organosulphur compounds) are quantitatively transformed into SO_2 at the temperatures needed for methane oxidation [8].

2. Experimental

2.1. Preparation of catalysts

The catalyst supports used in this work were $\gamma\text{-Al}_2\text{O}_3$ (BASF, $228.8\text{ m}^2\text{ g}^{-1}$), SiO_2 (BASF, $160.4\text{ m}^2\text{ g}^{-1}$), TiO_2 (Anatase, Degussa-Hüls, $49.1\text{ m}^2\text{ g}^{-1}$), $\text{ZrO}_2\text{-Y}$ (TOSOH Corporation, 5.14 wt.% Y, $11.7\text{ m}^2\text{ g}^{-1}$), $\text{ZrO}_2\text{-La}$ (MELCAT, 10 wt.% La, $281.8\text{ m}^2\text{ g}^{-1}$), and pure ZrO_2 prepared by calcining at 700°C of pure hydroxide also supplied by MELCAT ($318\text{ m}^2\text{ g}^{-1}$).

Supported Pd catalysts were prepared by incipient wetness impregnation of the supports at room temperature. Two com-

mercial precursors are commonly used: $\text{Pd}(\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$ and PdCl_2 . As chloride anions are considered a poison for the catalysts, when PdCl_2 is used as a precursor, a wash step is necessary in order to eliminate them [6]. On the other hand, it is known that $\text{Pd}(\text{NO}_3)_2$ leads to catalysts with higher crystallite size and lower metal dispersion, although more active for the oxidation of methane [16]. For this reason, it was selected as the precursor. $\text{Pd}(\text{NO}_3)_2$ was dissolved both in water and also in aqueous solution of ammonia (to prevent coalescence) and butanol (to decrease surface tension and produce better wetting of the support). Metal concentrations were selected in order to achieve the desired final concentration of metal in the catalyst using the incipient wetness technique. It was found that this second solution provided poorer metal dispersion and catalyst performance, so aqueous $\text{Pd}(\text{NO}_3)_2$ was used as a precursor in all the experiments reported here.

The catalysts were dried overnight at 100°C after impregnation and then calcined in air at 550°C for 2 h. Chemical analysis (using ICP-MS) revealed that Pd loading of the prepared catalysts was close to 1 wt.% for all the materials studied in this work.

In previous works of our group [7], it has been observed that non-reduced palladium catalysts are more active than the reduced ones. For this reason, the calcined catalysts were used in the reactor without further reduction.

2.2. Characterisation of catalysts

Fresh and used catalysts were characterised by different techniques. The catalyst pore size distribution and surface area were measured by nitrogen adsorption at -196°C with a Micromeritics ASAP 2000 surface analyser, considering a value of 0.164 nm^2 for the cross-section area of the nitrogen molecule. All samples were outgassed at 200°C before analysis.

Temperature-programmed desorption analyses were carried out using a Micromeritics TPD/TPR 2900 Analyzer, operating at ambient pressure. The reactor was a quartz glass vertical tube and the catalyst samples (0.02 g) were kept in position by plugs of quartz wool. The reactor was placed inside an electric furnace, temperature being controlled by a PID controller (Eurotherm). The carrier gas was He and its flow rate (50 mL min^{-1}) was measured by a rotameter. The temperature was increased from room temperature to 900°C at $10^\circ\text{C min}^{-1}$, and the gas leaving the reactor was analysed by a mass spectrometer (GASLAB 300) in order to detect the release of the different compounds (SO_2 , SO_3 , O_2 , etc.).

Powder X-ray diffraction patterns for fresh and deactivated catalysts were recorded in a D-5000 Siemens diffractometer, using nickel-filtered $\text{Cu K}\alpha$ as monochromatic X-ray radiation. The patterns were recorded over a range of 2θ angles from 20° to 70° and crystalline phases were identified using JCPDS files.

2.3. Reaction studies

Experiments were carried out in a laboratory fixed-bed catalytic reactor, consisting of a 400 mm long and 9 mm internal diameter stainless steel tube. The reactor was loaded with

Table 1
Values of kinetic constant at 450 °C, activation energy and T_{50} for the studied catalysts in presence and absence of SO₂

Support	T_{50} (°C)	k_0 (mol h ⁻¹ g ⁻¹ bar ⁻¹)	E_a (kJ mol ⁻¹)	R^2
Al ₂ O ₃				
Without SO ₂	334	1.99×10^6	76.3	0.991
With 40 ppm SO ₂	490	1.24×10^9	123	0.996
TiO ₂				
Without SO ₂	483	1.54×10^6	78.7	0.983
With 40 ppm SO ₂	–	1.84×10^6	89.2	0.995
SiO ₂				
Without SO ₂	337	1.48×10^7	75.0	0.991
With 40 ppm SO ₂	–	2.25×10^{22}	340	0.994
ZrO ₂				
Without SO ₂	406	5.05×10^6	74.5	0.995
With 40 ppm SO ₂	484	4.70×10^7	100	0.995

0.06 g of catalyst, mixed with 1 g of inert glass spheres as diluent, placed in the middle section of the reactor. The top part was filled with additional inert glass spheres. The reactor was placed inside an electric furnace, the temperature being controlled by a PID controller (Honeywell) connected to a thermocouple situated inside the reactor, in the zone charged with catalyst. The system was provided with five additional thermocouples that measured the reactor wall temperature at different positions.

The reactor feed consisted of 1 N L min⁻¹ (controlled by a Brooks 5850 TR mass flow controller) of a mixture of methane (5000 ppmV) and SO₂ (40 ppmV) in synthetic air, resulting a WHSV of 268.8 min g (mol of methane)⁻¹. Both methane and sulphur concentrations are values in the range commonly found in off-gases, such as those produced in coke ovens or composting facilities [8]. The exhaust gas was analysed by gas chromatography (Hewlett Packard HP 5890 Series II). Partial oxidation products, such as CO, have not been detected in any experiment. In a preliminary experiment was observed that at reaction conditions and in absence of catalyst, methane conversion was negligible.

Two different kinds of experiments were carried out. The first set of experiments was devoted to the study of the activity of the different catalysts for methane oxidation by recording light-off curves for the oxidation of 2000 ppmV methane in air in presence of 40 ppm of SO₂. In these experiments, the reactor was loaded with 0.06 g of catalyst, corresponding to a space time of 22.4 g h mol⁻¹.

The second set of experiments was devoted to characterise the deactivation of the catalyst. The resulting activities were determined at 450 °C and a space time of 22.4 g h mol⁻¹.

3. Results and discussion

3.1. Light-off experiments

The performance of the home-made catalysts was tested by recording light-off curves and performing ageing experiments. Light-off experiments consisted of increasing the reaction temperature from 150 °C to 550 °C at 2 °C min⁻¹. Before starting

each light-off experiment, the reactor was maintained at 450 °C for 15 h in air. Values of the parameter T_{50} , defined as the temperature needed for achieving 50% conversion, obtained from light-off curves, are given in Table 1.

The kinetic controlled region of the light-off curves (conversions lower than 80%) was fitted to a first order kinetic model. Although it is accepted that the oxidation of methane over palladium catalysts follows Mars–Van Krevelen mechanisms [17], pseudo-first order models can be accurate enough and suitable for comparing the activities of different catalysts. So, considering first order dependence on methane concentration, zero order on oxygen concentration (due to its high and almost constant concentration), and Arrhenius dependence on temperature for the kinetic constant, the kinetic equations are the following:

$$(-r_A) = k p_A = p_{A0}(1 - x) \quad (1)$$

$$k = k_0 \exp \left\{ \frac{-E_a}{RT} \right\} \quad (2)$$

being $(-r_A)$ the reaction rate for methane combustion, p_A the partial pressure of methane, p_{A0} the partial pressure of methane in the reactor feed, k the kinetic constant (mol h⁻¹ g⁻¹ bar⁻¹), R the gas constant, T the absolute temperature, x the methane conversion, k_0 the pre-exponential factor and E_a the activation energy (kJ mol⁻¹). It must be pointed out that Eq. (1) neglects the change in density of the reactant gas associated to the reaction, which is true because of the high dilution of methane.

If plug flow-like behaviour for the reactor is supposed and considering integral reactor, the following equation describes the behaviour the evolution of the conversion with the space time (τ):

$$\tau = \int_0^x \frac{dx}{-r_A} \quad (3)$$

Substituting Eq. (1) in Eq. (3), integrating, and putting the kinetic constant as a function of the temperature, the following linear expression is obtained:

$$\text{Ln}(-\text{Ln}(1 - x)) = \text{Ln}(k_0 \tau p_{A0}) - \frac{E_a}{RT} \quad (4)$$

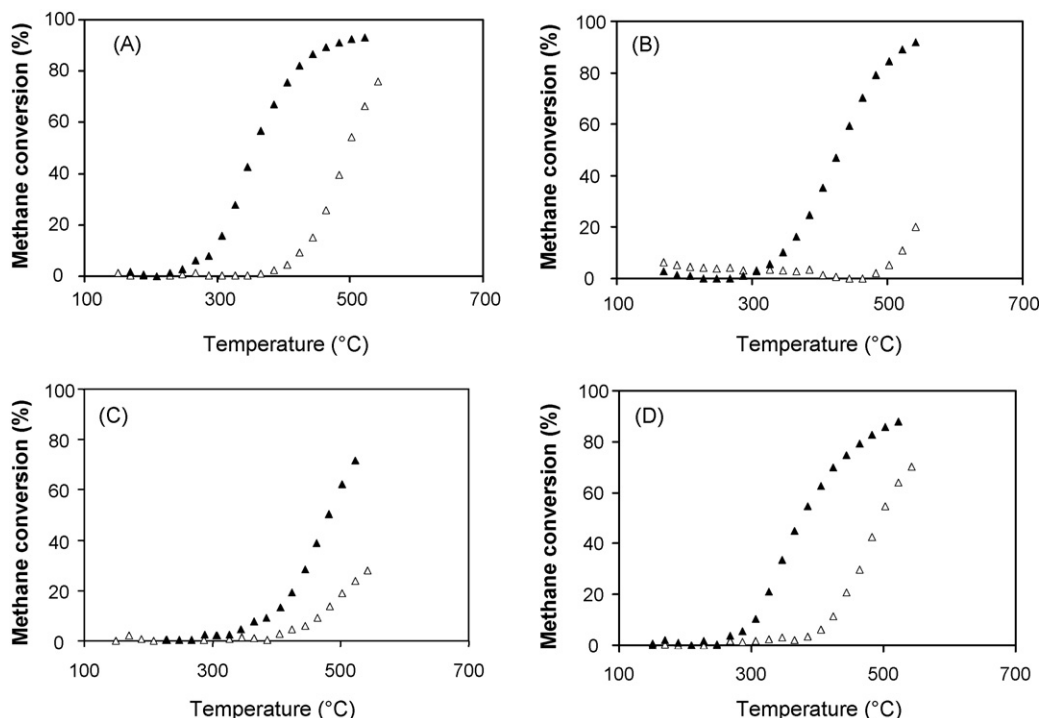


Fig. 1. Light-off curves (conversion vs. temperature) for the combustion of 5000 ppmV methane in air in without SO₂ (filled symbols) and in presence of 40 ppmV of SO₂ (open symbols). Light-off curves were recorded for 1 wt.% of Pd supported on Al₂O₃ (A), SiO₂ (B), TiO₂ (C) and ZrO₂ (D).

where Ln means the natural logarithm of the given expression, x is the fractional conversion of methane, τ is the space time (22.4 g h (mol of CH₄)⁻¹) and p_0 is the methane initial partial pressure (0.002 bar, neglecting temperature profiles inside the reactor).

The model parameters that are fitted to the experimental data are k_0 and E_a . Table 1 shows a summary of the results obtained.

Pd supported on both alumina and zirconia shows very similar behaviour (Fig. 1A and D, Table 1). Both catalysts show an important decrease of activity in presence of SO₂, but are still active at these conditions. However, the catalysts supported on titania and silica are much less active. Comparison of these results with those obtained for the same catalysts and reaction conditions, but with no sulphur compounds present, show that conversions decrease sharply in the presence of SO₂. So, T_{50} increases 140 °C and 80 °C for alumina and zirconia, respectively. This effect is even stronger for the silica-supported catalyst, which showed similar activity than the alumina- and zirconia-supported in the absence of SO₂, whereas in the presence of SO₂ provides the lowest conversions. By contrast, the effect of the SO₂ is less marked for the TiO₂-supported catalyst, which is the support leading to the less active catalysts in absence of SO₂.

The decrease of activity detected in these experiments is caused by both inhibition effects and catalyst deactivation. The last cause will be studied in more detail in the following set of experiments. So, inhibition effects cause a decrease in the conversion (if compared with experiments without SO₂) but with stationary conversions, whereas poisoning effects will lead to a continuous decrease of the catalyst activity.

3.2. Ageing experiments

Ageing experiments were carried out for 16 h at a constant temperature of 450 °C (Fig. 2). This temperature was chosen because it is in the range needed for methane combustion, and because it was observed in previous methane combustion experiments that self-deactivation of the studied catalysts is not important at this temperature [8]. The space time and concen-

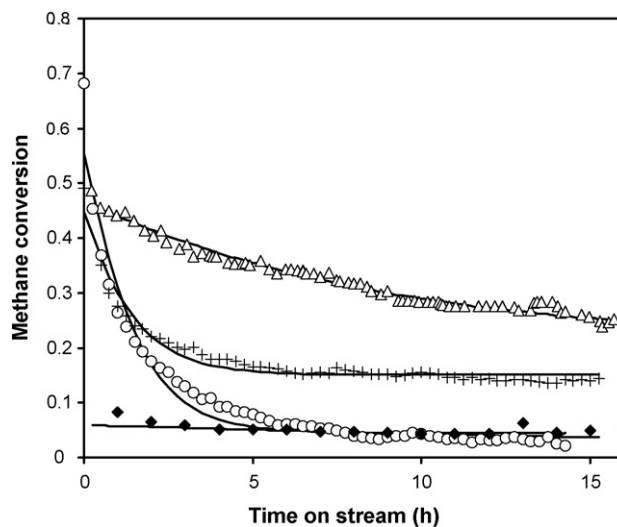


Fig. 2. Ageing curves (conversion vs. time on stream) for the oxidation of 5000 ppmV of CH₄ in presence of 40 ppmV of SO₂ for 1 wt.% Pd supported on: ZrO₂ (Δ), Al₂O₃ (+), TiO₂ (\circ), and SiO₂ (\blacklozenge). Lines correspond to prediction of the proposed deactivation model (Table 2).

Table 2
Values of the kinetic constants of the deactivation model for the studied supports

Support	k_1 (mol h ⁻¹ g ⁻¹ bar ⁻¹)	k_2 (mol h ⁻¹ g ⁻¹ bar ⁻¹)	j' (h ⁻¹)	R^2
Al ₂ O ₃	26.6	7.3	0.020	0.996
TiO ₂	36.2	2.1	0.021	0.972
SiO ₂	2.73	0	8.1×10^{-4}	0.981
ZrO ₂	27.9	10.4	0.0033	0.998

trations used in these experiments are the same than the used in the recording of the light-off curves. Experimental results show that the catalyst supported on ZrO₂ presents the higher thioreistance, followed by the catalyst supported on alumina. The catalysts supported on both titania and silica present very poor performance (conversions lower than 10%).

Deactivation behaviour could be better explained in terms of fitting parameters of a deactivation model. So, in a previous work of our group, a deactivation model has been developed and experimentally validated at different temperatures and SO₂ partial pressures for a commercial Pd/Al₂O₃ catalyst [18]. According to this model, we can define the parameter Φ as the fraction of Pd active sites that are in the form of sulphur-poisoned palladium (surface sulphates or sulphites) at a given time, the reaction rate for the methane disappearance ($-r_A$) will be given by the equation:

$$(-r_A) = k_1(1 - \Phi)p_A + k_2\Phi p_A \quad (5)$$

where k_1 and k_2 are the kinetic constants for the methane oxidation over the oxidised and sulphur-poisoned centres, respectively, and p_A is the methane partial pressure. If Eq. (5) is integrated considering plug flow reactor, Eq. (6) is obtained:

$$\tau = \int_0^{x_A} \frac{dx}{-r_A} = \frac{1}{p_{A0} [k_1(1 - \Phi) + k_2\Phi]} \text{Ln} \left(\frac{1}{1 - x} \right) \quad (6)$$

Eq. (6) considers that the catalyst conditions do not depend on the reactor position. This assumption is reasonable considering that the catalyst bed is short (0.5 cm) and the adsorption and reaction of the sulphur compound is fast. Sulphur dioxide concentration is also considered constant. These assumptions are common in simplified models for deactivating catalysts [19,20].

From Eq. (6), it is possible to obtain an explicit expression of Φ , as a function of methane conversion and the kinetic parameters:

$$\Phi = \frac{1}{k_1 - k_2} \left[\frac{\text{Ln}(1 - x)}{\tau p_{A0}} + k_1 \right] \quad (7)$$

As time on stream increases, the parameter Φ increases, from $\Phi = 0$ at $t = 0$, to $\Phi = 1$ at time on stream high enough for considering the active surface completely saturated of sulphur.

Considering that the sulphur poisoning of the catalyst, and hence the increase of Φ , takes place by reaction between the sulphur compound and the non-sulphated surface Pd atoms, the reaction rate for this process would be given by:

$$\frac{d\Phi}{dt} = j(1 - \Phi)^n p_S^m \quad (8)$$

where t is the time on stream (h) and p_S is the partial pressure of sulphur oxide at the reactor inlet (bar). The orders n and m can be taken as $n = m = 1$ as first approach [18]. Considering that all the experiments were carried out at the same concentration of SO₂, and the concentration of SO₂ can be considered constant along the reactor, it can be defined a new constant $j' = j p_S$.

The proposed model (Eqs. (7) and (8)) was fitted to the experimental data, calculating the parameters k_1 , k_2 and j' , for the studied catalysts using the program Scientis. Deactivation kinetic constants are reported in Table 2.

According to the values of the deactivation kinetic constants, three different behaviours could be distinguished: Al₂O₃- and TiO₂-supported catalysts present analogous deactivation behaviour with similar values of the poisoning rate. By contrast, ZrO₂-supported catalyst present two important differences, the completely poisoned catalyst is more active, and the poisoning rate is one order of magnitude lower than the corresponding to the other two supports. SiO₂-supported catalyst is severely deactivated once is exposed to the sulphur compound (as observed in the light-off curve). Therefore, the poisoning rate is meaningless for this catalyst.

In order to investigate the effects of sulphur compounds on the different catalysts, temperature programme desorption experiments were carried for the used samples, using helium as carrier gas. The outlet gas was analysed by a mass spectrometer, in order to follow the evolution of the gaseous products released by the sample. In all the cases, the only sulphur product evolved was SO₂. The SO₂ release profiles for the different supports are shown in Fig. 3. Neither methane nor carbon oxidation products (CO or CO₂) were detected. This fact is in a good agreement

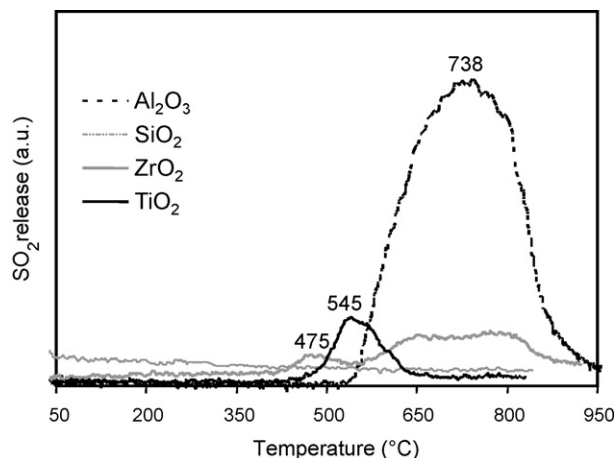


Fig. 3. Temperature-programmed desorption patterns for the studied catalysts after the poisoning experiment (SO₂ release).

with findings of other authors [21], who stated that the adsorption of methane on Pd is very weak. Oxygen releases were not observed for all the catalysts studied. This result, also observed for commercial Pd/Al₂O₃ catalyst [11], suggests the formation of surface sulphites, rather than sulphates, whose decomposition produce a simultaneous release of O₂ and SO₂.

Regarding the SO₂ releases, different supports present quite different behaviours. Alumina presents a large peak, starting at around 550 °C and finishing at around 900 °C, with the maximum at 738 °C. Titania shows a much smaller peak with a maximum at 545 °C, and zirconia shows a very small peak at around 475 °C, and a second wide peak at the same temperature interval that alumina, but much smaller. Silica does not present any noticeable desorption peak. These results suggest that the supports play a key role in the processes leading to the sulphur poisoning. The most of the SO₂ released during the TPD corresponds to sulphur associated to the support (the most severely poisoned catalysts does not show any SO₂ release). Thus, it could be inferred that zirconia, alumina and titania react with SO₂ during the reaction, forming surface sulphur species, and acting as sinks of SO₂ and hence avoiding to some extent that palladium reacts with SO₂-yielding palladium sulphate. This would explain the fastest deactivation showed by the silica-supported catalyst, and is in agreement with previous studies showing that Pd on sulphatable supports deactivates more slowly and can tolerate higher concentrations of SO₂ than on non-sulphating supports [22]. On the other hand, the catalysts that show the best thioreistance are those with larger desorption peaks (alumina and

zirconia supported). Concerning to the best performance of the ZrO₂-supported catalysts; it must be considered that zirconia-supported catalyst present best performance even in the absence of sulphur compounds. This differential behaviour is explained in the literature considering both the lower thermal stability and the higher thermal conductivity of the alumina [23].

In order to reveal possible changes in the support morphology and crystalline structure or to detect the formation of new compounds such as palladium sulphate, deactivated catalysts were also characterised by other techniques, such as XRD and BET. XRD profiles, recorded for the fresh and used samples, are shown in Fig. 4. Palladium phases were not observed (as expected considering the low concentration of active phase), except in the case of the SiO₂-supported catalysts. In this case, the (1 1 1) diffraction peak of the PdO phase is observed, remaining identical in the poisoned catalysts. It must be considered that the sulphite species will be formed in the surface of the crystallite, rather than in the bulk.

Concerning the supports, alumina is present in γ form, no noticeable differences between the fresh and deactivated profiles being found. At this point, it must be taken into account that the time on stream of this material is lower than the reported in the literature for observing support thermal sintering [8]. At this reaction times alumina phase transformations take place only at a surface level, not detectable using XRD. Titania support is formed by a mixture of two phases: anatase and rutile, and the zirconia support presents mainly its more stable phase (monoclinic ZrO₂, also called Baddeleyite), with small amounts of the

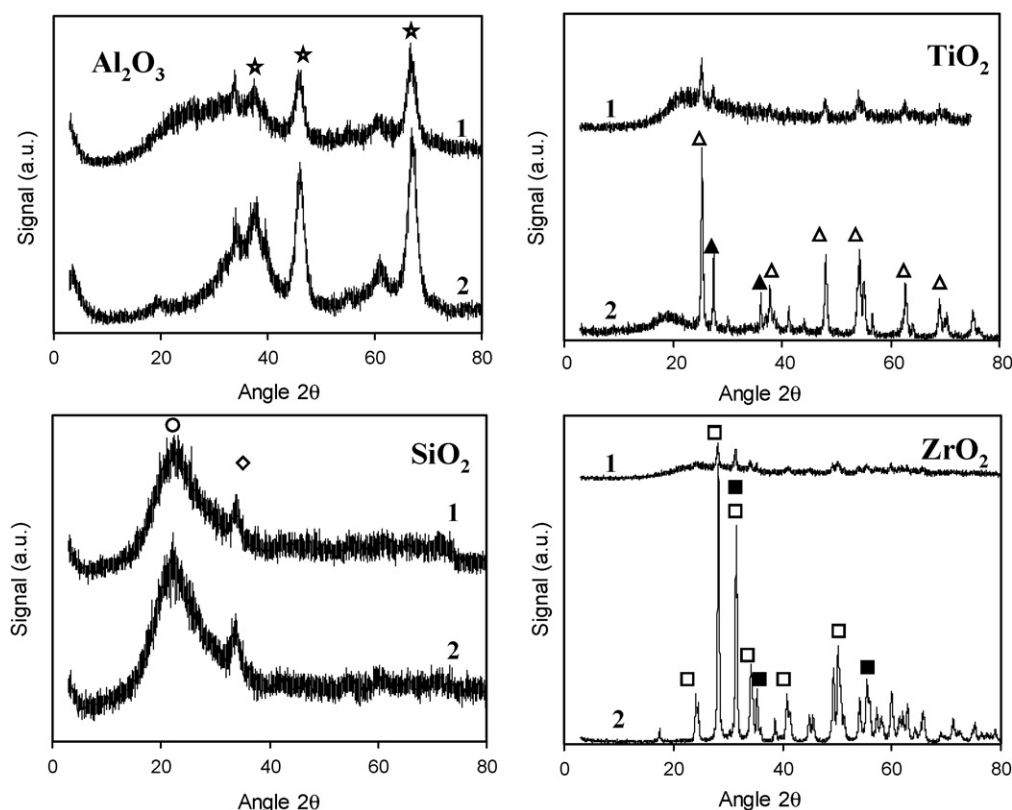


Fig. 4. XRD patterns for the sulphur-poisoned catalysts (profile 1) in comparison with those obtained for the fresh catalysts (profile 2). The main peaks are identified according to the legend: γ -Al₂O₃ (★), anatase (△), rutile (▲), amorphous silica (○), PdO (◇), tetragonal ZrO₂ (■) and monoclinic ZrO₂ (□).

tetragonal phase. The only observed alteration of these supports during the reaction was a marked crystallinity decrease.

Surface analyses of the materials do not reveal changes in the surface area, indicating that morphological changes of the support do not play any role in catalyst deactivation.

3.3. Modified zirconia supports

The modification of the catalyst properties by addition of promoters, in order to improve properties such as activity, selectivity, thermal stability or resistance to poisons is widely used in the preparation of industrial catalysts. For example, the addition of promoting agents (usually metals or metal oxides) is widely used in catalyst processes such as hydrogenations, isomerizations or partial oxidations [24,25]. Although in many cases the mechanisms are not well understood, alloying phenomena and modification of the properties of the support are considered as the most important phenomena taking place. Regarding to combustion catalysts, cerium, lanthanum and zirconium-modified Pd/Al₂O₃ catalysts are reported to present better performance than unmodified Pd/Al₂O₃ for methane deep oxidation [26]. Although these modified catalysts often present higher selectivity for intermediate products (which is not good for environmental purposes), the authors of the aforementioned work claim that no CO is formed with their modified catalysts. So, we observed in our previous work [7] that the modification of the Pd/ZrO₂ with Y lead to more active catalysts for catalytic combustion of lean methane emissions. However, there are not available data about the effect of these modifications on the resistance of these catalysts to sulphur poisoning.

According to the results shown in the previous section, zirconia showed the best performance in presence of SO₂ among the supports tested. In order to study the effect of promoters on the thioresistance of the catalyst, two commercial modified zirconia supports were tested: ZrO₂-Y (5.14 wt.% Y) supplied by TOSOH Corporation (11.7 m² g⁻¹) and ZrO₂-La (10 wt.% La) by MELCAT (281.8 m² g⁻¹). Both supports were impregnated with Pd, following the same procedure indicated in Section 2.1, and the catalysts produced were tested for the combustion of methane at the same operation conditions than in Sections 3.1 and 3.2.

The results of the light-off experiments are represented in Fig. 5 and the corresponding values of T_{50} , kinetic constants

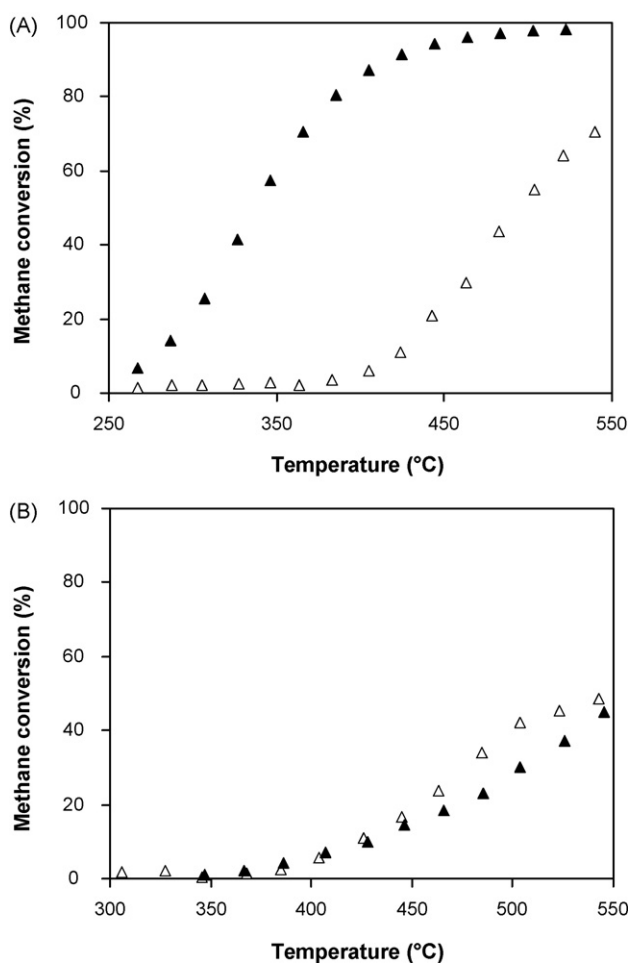


Fig. 5. Light-off curves (conversion vs. temperature) for the combustion of 5000 ppmV methane in air in without SO₂ (filled symbols) and in presence of 40 ppmV of SO₂ (open symbols). Light-off curves were recorded for 1 wt.% of Pd supported on Y-modified ZrO₂ (A), and La-modified ZrO₂ (B).

and activation energies are shown in Table 3. Although the Y-modified catalyst performs better than the non-modified catalyst in absence of SO₂, it seems more prone to sulphur poisoning. So, the activities of ZrO₂ and Y-modified ZrO₂ in presence of SO₂ are very similar. Concerning the addition of La, the resulting catalyst is less active than the other ZrO₂-based catalysts, although the effect of poisonous effect of the sulphur is slighter.

Table 3
Values of pseudo-first-order kinetic constants and T_{50} for the modified zirconia catalysts studied in this work in presence and absence of SO₂

Support	T_{50} (°C)	k_0 (mol h ⁻¹ g ⁻¹ bar ⁻¹)	E_a (kJ mol ⁻¹)	R^2
ZrO ₂				
Without SO ₂	406	5.05×10^6	74.5	0.995
With 40 ppm SO ₂	484	4.70×10^7	100	0.995
ZrO ₂ -Y				
Without SO ₂	383	2.01×10^7	77.0	0.992
With 40 ppm SO ₂	497	7.07×10^7	104	0.991
ZrO ₂ -La				
Without SO ₂	626	7.98×10^5	80.5	0.981
With 40 ppm SO ₂	–	2.42×10^8	113	0.977

Table 4

Values of the kinetic constants of the deactivation model for the zirconia-based studied supports

Support	k_1 (mol h ⁻¹ g ⁻¹ bar ⁻¹)	k_2 (mol h ⁻¹ g ⁻¹ bar ⁻¹)	j' (h ⁻¹)	R^2
ZrO ₂	27.9	10	0.0033	0.998
ZrO ₂ -Y	22.6	7.8	0.0071	0.998
ZrO ₂ -La	12.9	7.38×10^{-16}	8.1×10^{-4}	0.997

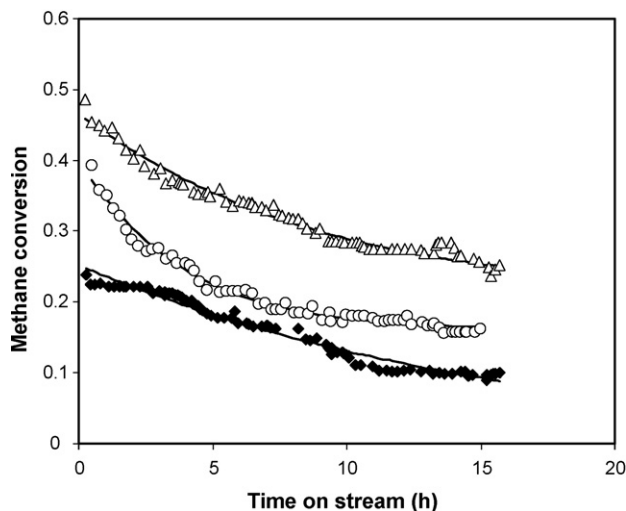


Fig. 6. Ageing curves (conversion vs. time on stream) for the oxidation of 5000 ppmV of CH₄ in presence of 40 ppmV of SO₂ for 1 wt.% Pd supported on: ZrO₂ (Δ), Y-modified LaO₂ (○), and La-modified ZrO₂ (◆). Lines correspond to prediction of the proposed deactivation model (Table 4).

Fig. 6 shows the results obtained in the ageing experiments, whereas Table 4 shows the fitting results using the proposed deactivation model. It can be observed that the modified supports show lower thioreistance, as observed in the higher deactivation rate for the Y-modified material, whereas La-modified material performs in a different fashion than the other studied supports, showing a continuous (almost linear) deactivation.

4. Conclusions

Palladium supported on zirconia shows similar activity for methane combustion, and higher resistance to poisoning by SO₂ than conventional Pd supported on alumina. This result is very interesting in order to develop total combustion catalysts able to work in presence of sulphur compounds, which is important from an environmental point of view. The addition of Y or La to the support, at the concentration tested, does not improve the performance of the catalysts.

Deactivation behaviour is accurately described by a deactivation model considering two different active sites (poisoned and non-poisoned), considering the poisoning reaction as a function of the sulphur concentration and the non-poisoned sites concentration.

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