Catalysis Today 155 (2010) 59–65

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Study of sulfur poisoning on Pd/Al_2O_3 and $Pd/CeO_2/Al_2O_3$ methane combustion catalysts

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ARTICLE INFO

Article history:
Available online 31 March 2009

Keywords:
CH_4 combustion
Pd catalysts
Cerium oxide
Sulfur poisoning

ABSTRACT

In the present work the CH_4 combustion behavior of Pd/Al_2O_3 and $Pd/CeO_2/Al_2O_3$ catalysts in the presence of SO_2 is investigated under various reaction conditions. Attention is paid also to the behavior of the bare supports without the active phase. Both fresh and poisoned samples are characterized by IR spectroscopy and *in situ* CO adsorption. Transient activity measurements after SO_2 poisoning indicate that regardless of CeO_2 loading a strong deactivation of all catalysts is observed compared to fresh samples. The effect of sulfur poisoning on steady state activity at 653 and 873 K is also measured. The deactivation is evident only at 653 K and its dynamics reflects the dynamics of SO_2 adsorption. Results of TPD experiments under inert or reaction atmosphere suggest that the dynamics of SO_2 desorption is influenced by the combustion reaction taking place on the catalyst active sites. Ceria-doped catalysts are more sensitive to the composition of the atmosphere of adsorption/desorption and quantitative measurements indicate that the presence of CeO_2 inhibits SO_2 adsorption under reaction conditions.

1. Introduction

Catalytic combustion of methane is an attractive way to produce thermal energy of high quality by burning efficiently at temperature lower than in conventional flame combustors and with less undesired noxious by-products [1]. In addition, methane has been used as a model compound for catalytic removal of diluted organic vapors due to the difficulty of oxidation and to its important greenhouse effect [2]. The use of natural gas fuelled vehicles (NGVs), in which unburned methane is emitted in the exhausts, poses additional issues related to the design of catalytic materials able to resist to poisons present in the exhaust gases and to exhibit high activity at the lowest temperatures.

Supported palladium oxide is the most active catalyst for complete methane oxidation [3] and it has been shown that its chemistry and reactivity can be modified by the choice of a proper support/promoter combination [4–6]. Metal oxides with high surface area such as Al_2O_3 are recognized to be the most suitable supports, since they can enhance catalytic activity [7]. Ceria is well known for its oxygen storage properties that are widely exploited in three way catalysts [8] and it has been reported to be an effective dopant also for supported palladium catalysts [9,10].

Under operating conditions, palladium-based catalysts can be poisoned and deactivated by several factors. Among the many causes of deactivation, poisoning by traces of sulfur compounds is one of the most relevant [11] especially in natural gas fuelled vehicles. Poisoning of Pd-based catalysts by sulfur compounds has been investigated in several works [12–21]. In these studies poisoning was carried out by exposing the catalysts either to SO_2 or to H_2S, although, due to conversion of H_2S to SO_2 under reaction conditions, the deactivation behavior displays similar characteristics [19,21]. IR spectroscopy [12,15,17,18] and XPS analysis after poisoning [13] showed the presence of surface sulfate species that are likely to be responsible for Pd deactivation.

Different mechanisms have been proposed for this deactivation. Lampert et al. [14] divided the supports in sulfating (like Al_2O_3) and non-sulfating ones (such as SiO_2 and ZrO_2), suggesting that the first can act as a sort of sink for SO_3 spilling from PdO and protecting it from deactivation. Mowery and McCormick [17] reached similar conclusions suggesting that SO_2 adsorbed on PdO can migrate between the active phase and the support, thus leading to a relatively low deactivation of PdO. A few studies [16,17] focused also on the effects of the presence of water in the reaction mixture, evidencing that the deactivation of the catalysts is higher and occurs more rapidly when both water and SO_2 are present.

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doi:10.1016/j.cattod.2009.02.019

In addition to the studies regarding the sulfation of Pd–alumina systems, some authors investigated sulfur effects on ceria [22–26] and on Pd/CeO_2 [27–29]. CeO_2 readily forms sulfate compounds. Waqif et al. [23] identified surface and bulk sulfates on CeO_2, characterized respectively by IR bands in the 1400–1340 cm^{-1} range and by a broad band at 1200 cm^{-1}. The studies of Pd/CeO_2 systems show that catalytic activity is dramatically reduced after exposure to SO_2 and again the formation of bulk and surface sulfates has been detected. Only a few studies investigated the behavior of Pd/CeO_2/Al_2O_3; Beck et al. found that the presence of SO_2 in the feedstream canceled the improvement made by the addition of CeO_2 to the Pd/alumina system under simulated three-way operation [30]. Recently we have studied the reactivity of both fresh and sulfur poisoned Pd/Al_2O_3 and Pd/CeO_2/Al_2O_3 catalysts, proposing a regeneration treatment based on alternate CH_4-reducing/lean combustion pulses and evidencing a protecting role of CeO_2 on Pd poisoning [31,32]. In particular, it has been observed that in presence of CeO_2 the reactivation of sulfur poisoned samples by CH_4-reducing pulses is anticipated with respect to Pd/Al_2O_3 catalyst. This reactivation has been ascribed to the reduction and subsequent reformation of some unpoisoned PdO, suggesting that CeO_2 can protect this fraction of PdO during the exposure to an SO_2 containing flow and also from the spill-back of support sulfates.

Aim of this work is to further investigate the effect of sulfur poisoning and the deactivation phenomena occurring on both Pd/Al_2O_3 and Pd/CeO_2/Al_2O_3 catalysts by means of catalyst characterization, temperature programmed desorption (TPD) and reactivity studies under different atmospheres. Major attention has been paid to the role of CeO_2 by the comparative study of ceria-promoted samples with different CeO_2 loadings (0.5–25%) and of ceria-doped supports prior to Pd deposition. This can also give some more insights for the understanding of the mechanisms involved in the deactivation of Pd-based catalysts.

2. Experimental

2.1. Materials

The starting material was a γ-Al_2O_3 support (LaRoche Versal TD250), with BET surface area of 147 m^2/g after calcination at 1273 K. CeO_2-promoted samples were prepared by incipient wetness impregnation of alumina with a solution of $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich 99.99%) to obtain CeO_2 loadings of 0.5–25 wt%. Subsequently they were dried overnight at 393 K and calcined at 1273 K for 6 h under air flow. Structural and morphological properties of these supports have been investigated recently [33].

Catalysts containing 2 wt%. Pd were prepared by deposition of the metal on CeO_2/Al_2O_3 by incipient wetness technique using a solution of $Pd(NO_3)_2$ (Aldrich, 10 wt% Pd, 99.999%). Samples were subsequently dried overnight at 393 K and calcined for 6 h at 1073 K.

Textural properties of the materials were characterized by BET surface area measurements using a Sorptomatic 1990 porosimeter and XRD measurements were carried out with a Philips X'Pert diffractometer with Cu Kα radiation. IR spectra were recorded with 100 scans on a Fourier-transform spectrometer (Nexus from Nicolet) with a resolution of 4 cm^{-1}. Prior to measurement samples were evacuated for 1 h at 623 K. Composition and textural properties of samples are reported in Table 1.

2.2. Methods

Overall behavior of the catalysts in the presence of sulfur was studied monitoring adsorption (sulfation) and desorption of SO_2 under either reaction or under non-reactive (or inert) conditions, or a combination of the two. In the following the terms *reaction* (r) and *inert* (i) will always refer to the use of a reactive and non-reactive mixture, respectively. Temperature programmed desorption experiments were carried out by loading the samples (60 mg, particle diameter 50 μm < Ø < 100 μm) on a quartz wool bed in a tubular quartz reactor (i.d. 6 mm, *l* 300 mm). Before each adsorption/desorption treatment, a temperature programmed combustion (TPC) experiment (0.5% CH_4, 2% O_2 in He) was carried out in order to stabilize the behavior of the catalysts [34]; therefore the term "fresh samples" will refer to catalysts that have already performed a TPC cycle.

Table 1
List of samples with corresponding weight composition and surface area (referred to 1 g of sample and to 1 g of Al_2O_3).

	Composition (wt%)	BET surface area (m^2/g)	BET surface area (m^2/g of Al_2O_3)
Support			
Alumina	Pure Al_2O_3	147	147
0.5CeAl	0.5%CeO_2/Al_2O_3	138	139
3CeAl	3%CeO_2/Al_2O_3	142	146
15CeAl	15%CeO_2/Al_2O_3	123	145
25CeAl	25%CeO_2/Al_2O_3	109	145
Catalyst			
PdAl	2%Pd/Al_2O_3	122	124
Pd0.5CeAl	2%Pd/0.5%CeO_2/Al_2O_3	125	128
Pd3CeAl	2%Pd/3%CeO_2/Al_2O_3	113	119
Pd15CeAl	2%Pd/15%CeO_2/Al_2O_3	98	118
Pd25CeAl	2%Pd/25%CeO_2/Al_2O_3	94	129

Reaction sulfation (r) was carried out at two different temperatures (653 and 873 K) as follows: fresh catalysts were exposed overnight (for 15 h) to a mixture of 10 ppm SO_2, 2% O_2, 0.5% CH_4, balance He for a total flowrate of 0.18 Nl/min (GHSV = 180,000 h^{-1}). Oven temperature was kept constant while monitoring the effluent gases (CO, CO_2, CH_4, O_2 and SO_2) with ABB 2020 series gas analyzers. After this treatment samples were cooled down to room temperature in pure He.

Inert sulfation (i) was carried out by treating the samples overnight at 653 K in He with 10 ppm SO_2 and a total flowrate of 0.18 Nl/min followed by cooling in pure He. Desorption was carried out in a TPC reaction mixture of 2% O_2 and 0.5% CH_4 in He (r), or in pure He (i) by heating the catalysts up to 1173 K at a heating ramp of 10 K/min and then cooling them down at the same rate to room temperature. SO_2 desorption was quantitatively measured in both cases by UV adsorption (ABB Limas 11 analyzer). Catalytic activity (CO, CO_2, CH_4 and O_2) as a function of temperature was also monitored during reaction desorption.

3. Results and discussion

3.1. Catalysts characterization

Surface area data reported in Table 1 show that the addition of ceria decreases the surface area calculated on a per gram basis; this is a quite general behavior when adding a non-porous oxide to a high surface area support. If data are calculated on a gram of Al_2O_3 basis, surface areas do not show any significant variation within the entire composition range. This is in agreement with previous report [33], showing that CeO_2 does not affect textural properties of Al_2O_3 at a calcination temperature of 1273 K. The addition of the noble metal instead have a slightly detrimental effect on the surface area of the catalysts.

Infrared spectroscopy was used as a valid tool to characterize the surface of the samples in order to individuate surface species formed after the poisoning treatment. The study was carried out on

PdAl and Pd15CeAl samples that were chosen as representative of the entire set. In Fig. 1a the IR spectra for the fresh and poisoned catalysts in the 3000–4000 cm^{-1} range are shown. For all these samples SO_2 adsorption occurred under reaction conditions (0.5% CH_4, 2% O_2, 10 ppm SO_2 in He) at 653 K. In the 3800–3400 cm^{-1} range (OH stretching region) the PdAl sample exhibits bands at 3790, 3730 and 3684 cm^{-1} belonging to ν-OH on Al^{3+} ions at different coordination. The Pd15CeAl sample shows maxima at 3764, 3725 and 3673 cm^{-1}. SO_2 adsorption has produced in both catalysts a decrease of the intensity of the ν-OH bands, which is more pronounced for the ceria-containing sample. This means that sulfation likely occurred via chemisorption involving surface OH groups. A modification of OH stretching region after sulfation was observed also by Waqif et al. [35] on different metal oxides.

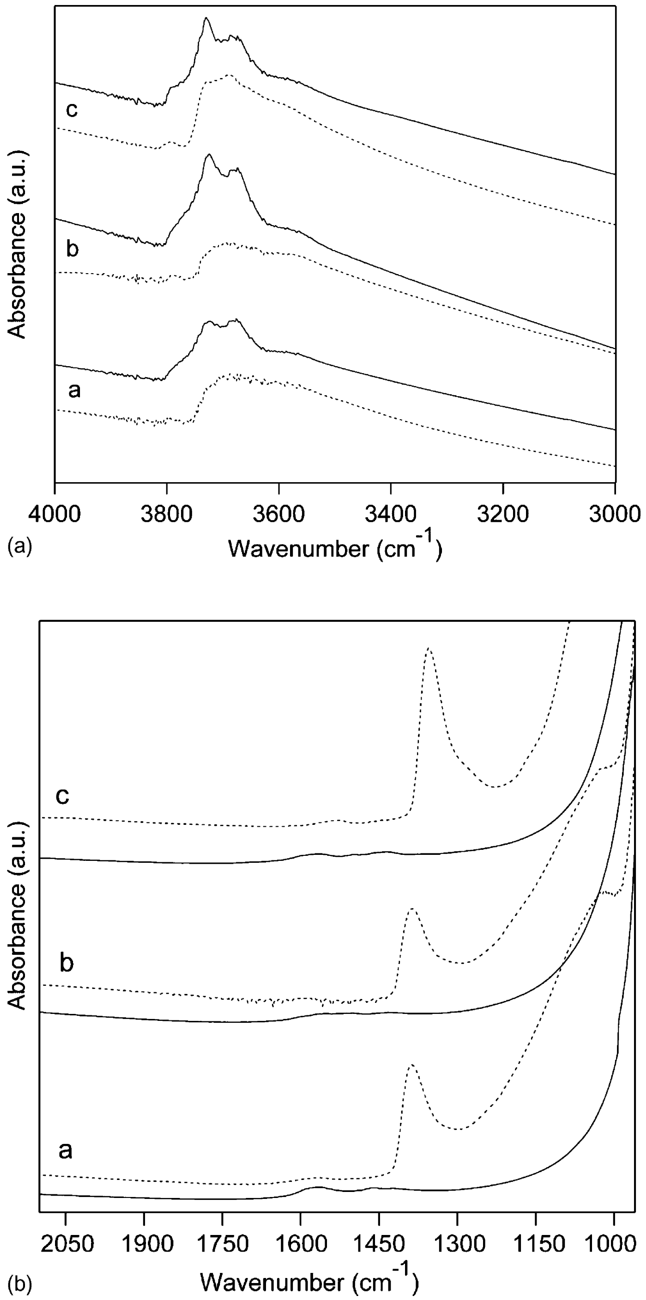

Fig. 1. (a) IR spectra of 15CeAl support (a), Pd15CeAl (b) and PdAl (c) catalysts fresh (solid line) and poisoned (dashed line) in the 3000–4000 cm^{-1} range. (b) IR spectra of 15CeAl support (a), Pd15CeAl (b) and PdAl (c) catalysts fresh (solid line) and poisoned (dashed line) in the 950–2200 cm^{-1} range.

In Fig. 1b the IR spectra of the fresh and poisoned catalysts recorded in the S=O stretching region (1500–1000 cm^{-1} range) are reported. The presence of sulfates is indicated by the band at about 1380 cm^{-1} (νS=O). According to Pieplu et al. [36] the peaks at 1380 and 1045 cm^{-1} can be attributed to surface sulfate species adsorbed on alumina. Waqif et al. [23] indicated that the bands between 1400 and 1340 cm^{-1} can be referred to surface sulfates on ceria, while the broad bands between 1200 and 1060 cm^{-1} are attributed to CeO_2 bulk sulfates. In our samples the presence of the latter bands is clearly distinguished and can be due to the saturation of the surface with subsequent formation of bulk sulfates in the presence of ceria. The same IR spectrum has been obtained also for the pure support 15CeAl, with no effect of the noble metal.

The absence of the band at 1435 cm^{-1} attributed to νS=O of $PdSO_4$ confirms that no stable sulfates are formed on Pd. The absence of $PdSO_4$ is reported also by Yu and Shaw [15], while Mowery and McCormick [17] observed the band at 1435 cm^{-1} in both supported and unsupported PdO by *in situ* IR measurements; in their experiments Pd loading for the supported catalysts was higher (6 wt%). Also Hoyos et al. [12] reported the presence of $PdSO_4$, but in their case the support was SiO_2 which is a non-sulfating support according to the observations made by Lampert et al. [14]. In our case the absence of $PdSO_4$ seems reasonable, due either to the low Pd loading and/or to the sulfating character of alumina support that can prevent the sulfation of PdO.

In situ CO adsorption was carried out for the characterization of Pd active sites. In Fig. 2 the spectra for PdAl and Pd15CeAl fresh and poisoned are shown. Fresh samples spectra are in perfect agreement with what reported in the literature for Pd–CO interaction [37]. The band at about 2095 cm^{-1} is attributed to linear Pd^0–CO complexes, while the broad band at 1950 cm^{-1} is ascribed to isolated $(Pd^0)_2$–CO complexes that are supposed to form on Pd (1 0 0) planes. On Pd15CeAl sample another band with maximum at 1995 cm^{-1} can be observed which is attributed to the presence of compressed bridged carbonyls that form on Pd (1 1 1) planes. This could mean that on 15CeAl support Pd is less dispersed than on pure alumina.

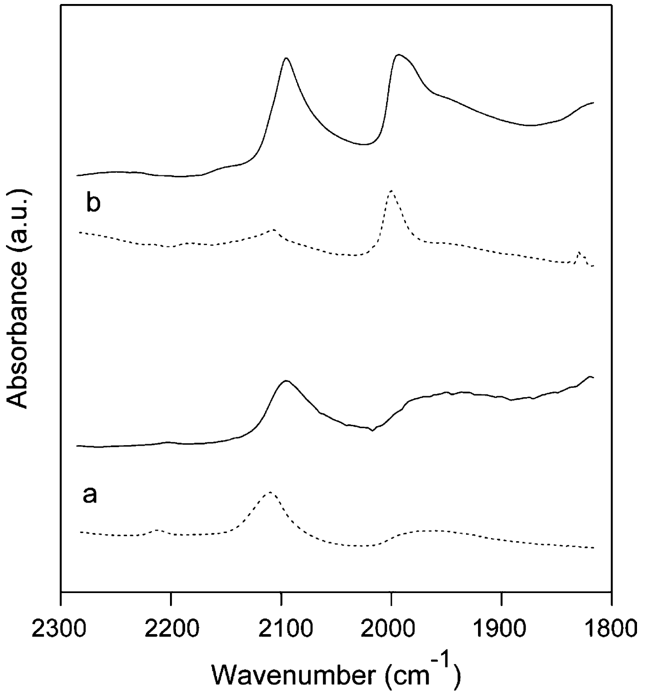

Fig. 2. IR spectra of PdAl (a) and Pd15CeAl (b) fresh (solid line) and poisoned (dashed line) after *in situ* CO adsorption.

Sulfation has a strong effect on the whole range of observed bands: there is a pronounced decrease of the band related to linear Pd^0–CO species, more evident for the ceria-doped sample, which moves to higher wavenumbers. This is likely due to the electron attractor effect of the SO_4^{2-} ions; probably Pd sites involved in this process have a partial positive charge. Isolated bridged carbonyls are more affected by the presence of SO_2, since their characteristic band has a lower intensity than in the fresh samples.

3.2. Reactivity studies

Reactivity tests were carried out in order to evaluate the effect of the addition of SO_2 in the gas stream on the catalytic activity of Pd-based samples, during both steady state and temperature programmed combustion experiments. The first step was the adsorption of SO_2 (sulfation) at a given temperature. During adsorption experiments under reaction conditions (0.5% CH_4, 2% O_2, 10 ppm SO_2 in He), the monitoring of CH_4 conversion as a function of time gave a measure of the deactivation of the catalysts due to SO_2 poisoning. In Fig. 3 curves of CH_4 conversion *vs.* time at two different temperatures are reported for PdAl and Pd15CeAl, for both fresh (a and b) and poisoned catalysts (a′ and b′). SO_2 breakthrough curves are also included together with methane conversion of the poisoned samples.

Looking at CH_4 conversion measured for the fresh samples (panels a and b) on a 15-h CH_4 combustion, it can be observed that both catalysts show a similar behavior, with a time-on-stream deactivation more pronounced at low temperature (653 K) compared to high temperature treatment (873 K). The addition of SO_2 in the reaction atmosphere at 653 K dramatically affects deactivation of both samples with time-on-stream, and it is interesting to observe that the dynamic of deactivation is strictly related to SO_2 adsorption. On Pd15CeAl SO_2 adsorption is faster than on PdAl, which in turn shows a slower decrease in CH_4 conversion. At 873 K the effect of sulfur poisoning on the deactivation is almost negligible, and the loss of conversion is close to that observed on the fresh samples deactivated during 15 h of CH_4 combustion in the absence of SO_2.

Temperature programmed combustion experiments for the fresh and poisoned PdAl and Pd15CeAl samples are shown in Fig. 4 along with SO_2 desorption curves. The T_{50} (the temperature at which 50% methane conversion is achieved) of the fresh samples in the absence of SO_2 is almost the same, 615 and 611 K for Pd15CeAl and PdAl, respectively. In the fresh catalysts the drop in conversion during the cooling part of the experiment, due to the decomposition of the active phase PdO to less active Pd metal, is reduced with the addition of ceria. CeO_2 promotes Pd reoxidation [9,10,38], thus narrowing the catalytic activity hysteresis observed during heating/cooling ramps. TPC curves on poisoned catalysts (Fig. 4, a′ and b′) show a pronounced deactivation during the heating ramp. At the same time, two SO_2 desorption peaks are observed: a low temperature peak (LT) at about 800 K and a high temperature peak (HT) at about 1100 K. The addition of ceria does not markedly affect the position of the peaks (i.e. the SO_2 desorption temperature), only a light anticipation of the L-T peak is observed, but markedly decreases the intensity of the H-T peak. After SO_2 desorption, catalytic activity is totally restored: CH_4 conversion during the cooling part of the cycle follows the same curve of the fresh catalysts. Also, a subsequent light-off experiment (not shown in the figure) is similar to the TPC of the fresh samples. This is partly in contrast with what observed by Lampert et al. [14], but it can be due to different experimental conditions (higher O_2 excess, monolith supported catalysts) and likely to the fact that in their case the second light-off curve in the sulfur-free mixture was performed with a maximum temperature of 923 K, below the HT SO_2 desorption peak.

3.3. SO_2 adsorption/desorption studies

Quantitative analysis for SO_2 adsorption (T = 653 K) and desorption for all experiments is reported in Table 2, with calculations referred to a catalyst unit surface area. These results are in agreement with the literature data where it is reported that the maximum amount of sulfate species produced on alumina after the interaction with SO_2 is below 2×10^{14} atoms/cm^2 [39]. In our case 1.1 μmol/m^2 of SO_2 adsorbed on alumina correspond to ca. 6.8×10^{13} atoms/cm^2. From quantitative analysis it appears that SO_2 desorption takes place almost completely during the heating ramp (the difference between adsorption and desorption is small and no SO_2 release is detected during cooling or during a second heating ramp) and this is in agreement with the total recovery in activity observed after the first light-off experiment of the

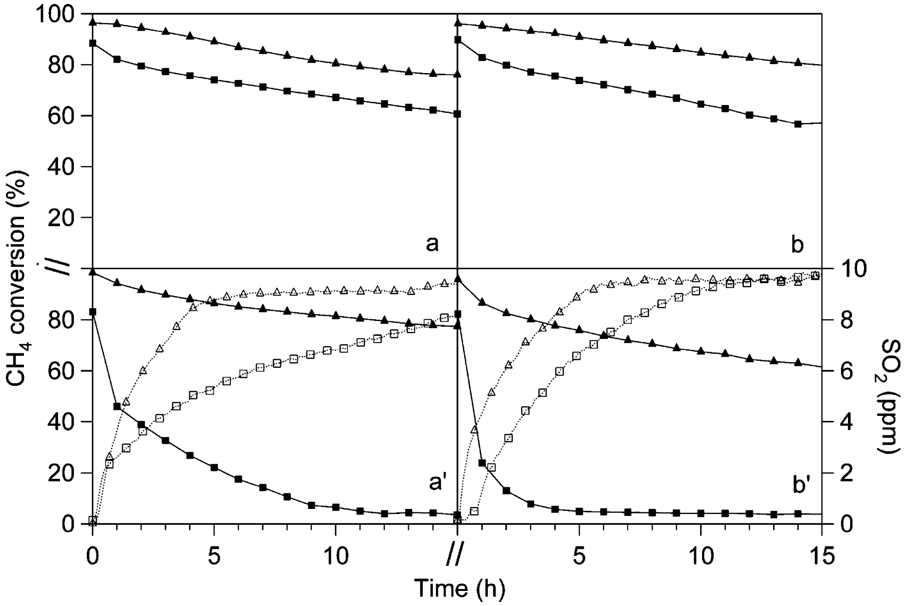

Fig. 3. Time-on-stream catalyst deactivation without SO_2 (a = PdAl and b = Pd15CeAl) and in presence of SO_2 (a′ = PdAl and b′ = Pd15CeAl) at 653 K (■) and 873 K (▲). SO_2 breakthrough curves for PdAl (a′) and Pd15CeAl (b′) at 653 K (□) and 873 K (△).

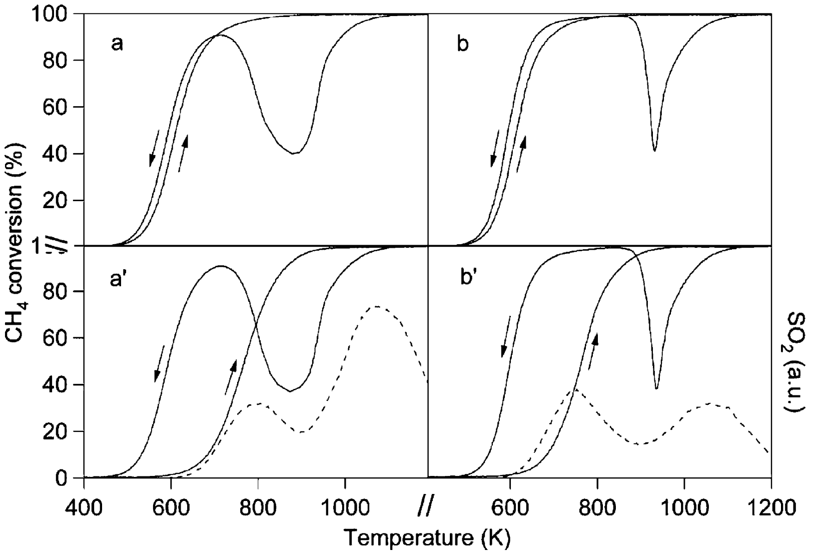

Fig. 4. CH_4 conversion on PdAl (a) and Pd15CeAl (b) fresh and PdAl (a′) and Pd15CeAl (b′) poisoned; heating and cooling profiles (solid line) and SO_2 desorption during heating (dashed line).

poisoned samples. The presence of the noble metal on pure alumina promotes SO_2 adsorption under reaction conditions (0.5% CH_4, 2% O_2, 10 ppm SO_2 in He), resulting in a higher degree of sulfation of the catalyst. Keeping into account that Pd promotes both SO_2 and H_2S oxidation, similar results were reported by Yu and Shaw [15] who observed an increased sulfation on Pd/Al_2O_3 with respect of pure alumina after exposure to H_2S. The addition of ceria on the alumina support enhances SO_2 adsorption due to the sulfation power of ceria [23]; the amount of SO_2 adsorbed increases with increasing ceria loading. When Pd is added to ceria-promoted alumina the amount of SO_2 adsorbed under reaction conditions is lower than that of Pd over pure Al_2O_3. This is in agreement with what reported by Boaro et al. [25] in a study on the influence of SO_2 on the OSC of ceria, who observed that the amount of SO_2 adsorbed on pure CeO_2 was higher than the amount adsorbed on Pd/CeO_2 catalyst.

To better understand the dynamics of SO_2 release and, in general, the role of ceria in the sulfation process, experiments were carried out on the doped supports without active phase (Fig. 5). Only one SO_2 desorption peak is observed in these samples (excluding 0.5CeAl that shows a very small peak at low temperature), that can be associated with the decomposition of bulk aluminum and/or cerium sulfates, both observed by IR characterization. As shown in Fig. 4, when Pd is present on the supports SO_2 desorption takes place in two steps, and the comparison of Figs. 4 and 5 implies that the LT SO_2 release peak is somehow related to the presence of Pd. This relationship could involve Pd directly via the formation of Pd sulfates (but on the basis of IR spectra, the formation of sulfates on Pd can be ruled out since no $PdSO_4$ has been detected) or indirectly, through the interaction of sulfates with reaction products mediated by the presence of Pd active sites. In particular, the presence of water as a product of combustion could be associated with the different dynamics of SO_2 release, since many authors have observed a strong relationship between water and the sulfation behavior of different materials [16,17,40,41].

Table 2
SO_2 amount adsorbed/desorbed per square meter of catalyst in different experimental conditions (*T* adsorption = 653 K).

Sample	Ads (μmol/m^2)	Des (μmol/m^2)
Reaction sulfation/reaction desorption		
Alumina	1.1	0.9
PdAl	3.9	3.4
0.5CeAl	1.1	1.0
3CeAl	2.2	2.0
15CeAl	2.8	2.5
25CeAl	3.2	2.8
Pd0.5CeAl	3.5	3.0
Pd3CeAl	3.1	3.0
Pd15CeAl	3.3	3.0
Pd25CeAl	3.6	3.3
Inert sulfation/inert desorption		
PdAl	3.8	3.6
Pd15CeAl	4.2	4.0
Inert sulfation/reaction desorption		
PdAl	4.2	4.0
Pd15CeAl	4.8	4.4
Reaction sulfation/inert desorption		
PdAl	4.1	3.9
Pd15CeAl	3.0	3.0

To further investigate this issue, experiments with a non-reactive mixture (10 ppm SO_2 in He) were carried out on PdAl and Pd15CeAl catalysts. Quantitative measurements for these experiments are included in Table 2 and the profiles of SO_2 release for

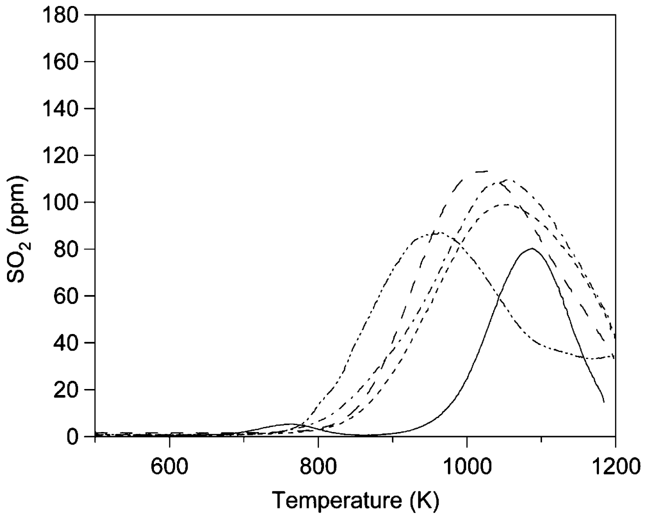

Fig. 5. SO_2 desorption (r) for CeAl samples ((—) 0.5CeAl, (– – – –) 3CeAl, (·–·–·) 15CeAl, (- - -) 25CeAl) and Al_2O_3 calcined at 1273 K (–··–··).

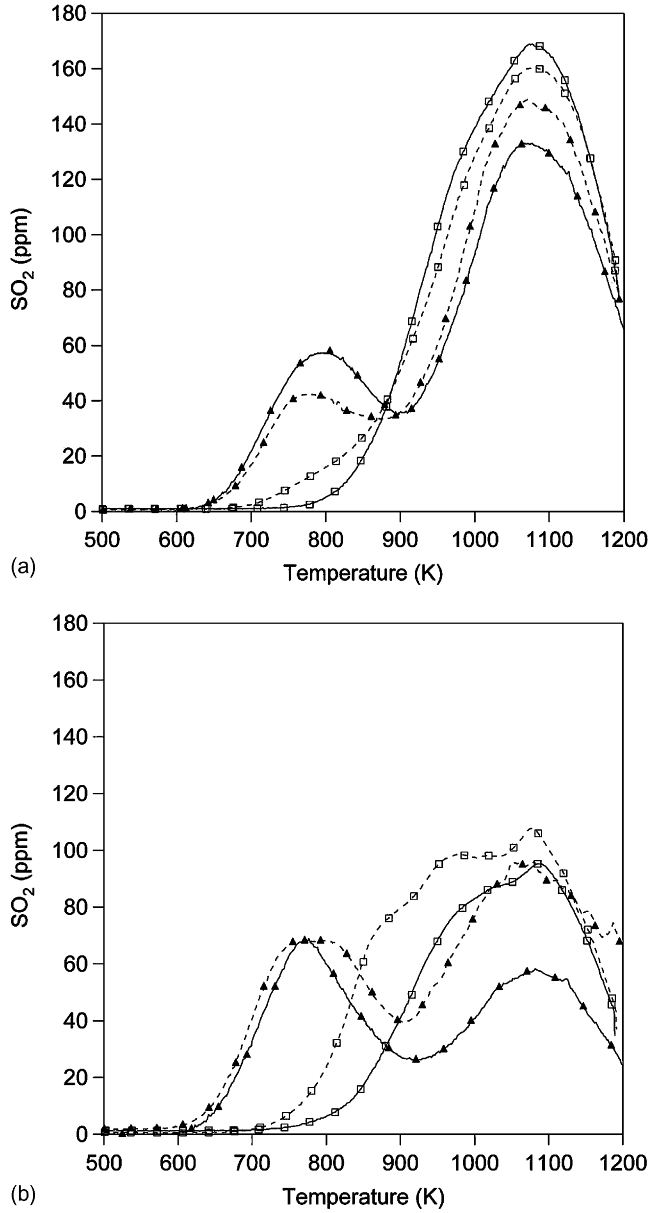

Fig. 6. (a) SO_2 desorption profiles for each type of experiment on PdAl sample (solid line: reaction sulfation; dashed line: inert sulfation; (▲) reaction desorption; (□) inert desorption). (b) SO_2 desorption profiles for each type of experiment on Pd15CeAl sample (solid line: reaction sulfation; dashed line: inert sulfation; (▲) reaction desorption; (□) inert desorption).

PdAl and Pd15CeAl are shown in Fig. 6a and b. From these results it is clear that the LT desorption peak is not strictly associated with Pd, since it is not observed in the presence of Pd with no reaction. Also Gélin et al. for Pd/Al_2O_3 [19] observed only one SO_2 desorption peak above 873 K in an atmosphere containing O_2 and He, i.e. without any combustion reaction.

A second series of experiments (also shown in Fig. 6a and b for PdAl and Pd15CeAl, respectively) was carried out on PdxCeAl samples with reaction sulfation (0.5% CH_4, 2% O_2, 10 ppm SO_2 in He; T = 653 K) and inert desorption (pure He) or with inert sulfation (10 ppm SO_2 in He; T = 653 K) and reaction desorption (0.5% CH_4, 2% O_2 in He). Note that the LT desorption peak is present only when the desorption is carried out under reaction atmosphere, irrespective of the adsorption conditions. It can be also observed that for PdAl catalyst there is no influence of the type of sulfation (inert or reaction) on the shape of desorption profiles nor on the amount of adsorbed/desorbed SO_2 (see Table 2). This is not the case of Pd15CeAl, where the inert adsorption leads always to a more complex SO_2 release profile and, more important, to a higher degree of sample sulfation (about 30% more than the reaction sulfation). This seems to be in agreement with what observed by Smirnov et al. [40], who reported that the presence of water hinders sulfate formation on pure CeO_2 with respect to an atmosphere containing SO_2 only.

On the basis of these results, it is clear that the presence of Pd alone cannot explain the low temperature SO_2 desorption peak, which in turn might be related to the production of water. In fact water is obviously absent during inert desorption as well as under reaction conditions over the pure supports which are not active for methane conversion in the temperature range investigated. Strong evidence of water–SO_2 interaction over a Pd/alumina catalyst was reported by Mowery et al. [16], who observed that the sulfation of the sample resulted in an increased amount of water adsorbed on the catalyst and proposed that water and SO_2 compete for adsorption sites on the surface. Analogously, Stenger et al. suggested that in the temperature range 300–800 K weakly adsorbed SO_2 on mordenite is replaced by more strongly adsorbed water [41], thus evidencing again a competing mechanism between the two species.

In order to better clarify this point, additional experiments were carried out by adding 1 vol.% of water to the flowing gas during inert adsorption (1% H_2O + 10 ppm SO_2 in He; T = 653 K) and desorption (1% H_2O in He). The amount of water corresponds to the stoichiometric amount produced during combustion under the conditions used in this work (0.5% CH_4, 2% O_2). The results reported in Fig. 7 show that the introduction of water in the feed does not affect SO_2 desorption in both catalysts. Therefore the dynamics of SO_2 desorption at low temperature is strictly connected with CH_4 activation and/or *in situ* production of water during combustion reaction on Pd sites. These sites, although not directly involved in the formation of bulk $PdSO_4$, appeared modified following poisoning under reaction conditions as checked by IR spectra of adsorbed CO. This means that only a combination of presence of Pd sites and onset of reaction allows to surface sulfates (mainly located on cerium and aluminum) to decompose at low temperature. This could help explaining why in our case SO_2 desorption starts in correspondence to the onset of catalytic reaction, i.e. when the production of water on the catalyst surface begins.

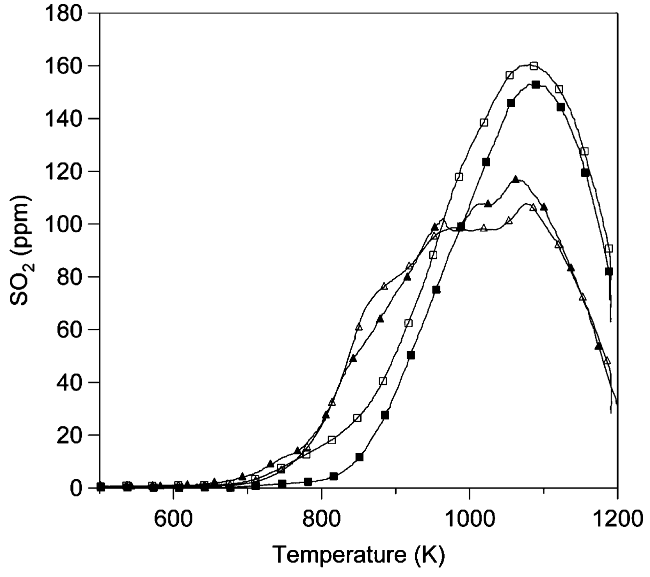

Fig. 7. SO_2 desorption profiles for PdAl (□■) and Pd15CeAl (▲△) samples; open symbols: inert sulfation, inert desorption; closed symbols: inert sulfation + 1 vol.% H_2O, inert desorption + 1 vol.% H_2O.

4. Conclusions

The sulfation of Pt-based catalysts promoted by ceria was investigated. IR spectra show that sulfation occurs via chemisorption involving surface OH groups. No $PdSO_4$ was detected, likely because alumina is a sulfating support and can prevent the sulfation of the active phase. Nevertheless, a decrease of the band related to linear Pd^0–CO species suggests some influence of SO_4^{2-} ions on Pd sites. On ceria-containing sample the formation of both surface and bulk sulfates was detected and a stronger interaction with the OH groups was observed. CO adsorption experiments evidenced a more pronounced decrease of the linear Pd^0–CO band on poisoned samples.

Steady state catalytic activity at 653 K is strongly influenced by the presence of SO_2 in the gas stream, leading to an almost complete loss in methane conversion in both doped and non-doped catalysts. For Pd15CeAl the deactivation is much faster than for PdAl sample, in agreement with the correspondent SO_2 adsorption dynamics. At 873 K SO_2 has almost no detrimental effect on steady state methane conversion.

Quantitative measurements of SO_2 adsorption/desorption show that the addition of CeO_2 on the alumina support inhibits sulfation under reaction atmosphere (0.5% CH_4, 2% O_2, 10 ppm SO_2 in He), in agreement with a previous work where a protecting role of CeO_2 on Pd has been evidenced [32]. In CeO_2-containing samples, the lower amount of SO_2 adsorbed under reaction conditions and the different SO_2 release profile observed when the adsorption is carried out in inert atmosphere (10 ppm SO_2 in He) show that the influence of water on SO_2 adsorption is stronger when ceria is present. For PdAl catalyst in fact, both the amount of SO_2 adsorbed and the shape of the SO_2 desorption peaks do not depend on the conditions of sulfation.

From the analysis of SO_2 desorption profiles under different atmospheres, it has been shown that the presence of water formed during combustion reaction has a strong influence on SO_2 adsorption/desorption dynamics. Summarizing: (i) in the absence of combustion reaction SO_2 desorption takes place in only one high temperature step, irrespective of the nature of the support and of the atmosphere of sulfation; (ii) on the other hand, the atmosphere of sulfation has a strong influence on the amount of SO_2 adsorbed on the ceria-doped catalyst. These evidences and comparison with previous literature results suggest that the first step of SO_2 desorption under reaction atmosphere can be related to a surface mechanism that involves PdO active sites for CH_4 activation and/or *in situ* production of water.

Acknowledgment

This work has been financially supported by MIUR (Italy) under PRIN projects.

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