Catalysis Letters Vol. 100, Nos. 1–2, March 2005 (© 2005)
DOI: 10.1007/s10562-004-3081-1

Methane catalytic combustion over Pd/Al_2O_3 in presence of sulphur dioxide: development of a regeneration procedure

Salvador Ordóñez*, Paloma Hurtado, and Fernando V. Díez

Department of Chemical and Environmental Engineering, University of Oviedo, Julián Clavería s/n, 33006 Oviedo, Spain

Received 01 October 2004; accepted 28 October 2004

Five different procedures (treatments with hydrogen, nitrogen, wet and dry air, and under vacuum) were tested for the regeneration of a partially deactivated alumina-supported Pd catalyst, used for the catalytic incineration of methane in presence of SO_2. The efficiency of these processes was evaluated considering the temperatures at which both, the catalysts deactivation, and the regeneration processes, took place. As general trend, hydrogen treatment is the best regeneration procedure, followed by treatment with wet air, whereas high deactivation temperatures lead to less efficient regeneration. The efficiency of the regeneration was observed to increase as regeneration temperature increases. These trends are discussed according to the results obtained in the characterisation of deactivated catalyst samples using TPR, TPO and TPD.

KEY WORDS: catalyst regeneration; sulphur poisoning; methane combustion; palladium catalysts.

1. Introduction

Catalytic combustion has become a very interesting alternative for the treatment of gaseous emissions containing diluted organic compounds, because of its low energy consumption (especially if compared with thermal oxidation) and the very small formation of noxious by-products, such as thermal NO_X [1,2].

Among the organic compounds present in gaseous emissions, methane is receiving increasing attention. This interest is justified by two considerations: on the one hand, methane is an important contributor to the greenhouse effect (its global warming potential is 21 times higher than that of carbon dioxide); on the other hand, the catalytic oxidation of methane is more difficult than for most volatile organic compounds [3]. Thus methane has been chosen by many authors as a model compound for catalytic oxidation studies, as the catalytic combustion of most organic compounds would be ensured if methane is quantitatively abated.

In many gaseous emissions (i.e., from carbochemical and petrochemical processes, treatment of solid wastes and wastewaters, motor vehicle exhaust gases, etc.), methane is accompanied by other inorganic (CO, CO_2, NO, H_2, H_2O, NH_3, H_2S, SO_2, etc.) and organic compounds (alkanes, alkenes, aromatics, etc.). Among these compounds, it was demonstrated in previous studies that sulphur compounds (SO_2 and H_2S) play a key role in the deactivation of the catalysts used for methane combustion [4,5]. Moreover, the conventional sulphur trapping systems are not efficient enough for the total removal of sulphur compounds, as pointed out in the literature [6].

The complete catalytic oxidation of methane can be performed over both, noble metals and transition metal oxides. Both families of catalysts have been studied extensively in order to develop catalytic combustion applications. The main advantage of noble metals over metal oxides is their superior specific activity, which makes them the best candidates for low-temperature combustion of hydrocarbons [7]. This is especially important in the case of methane, because, as indicated previously, it is the most difficult hydrocarbon to activate. Among noble metal catalysts, Pd is generally considered in the literature as the best option [7, and references cited therein]. Besides this, although it is known that Pd is very sensitive to sulphur poisoning [7,8], previous results of our research group showed that the activity of a sulphur-poisoned Pd for methane oxidation was higher than that corresponding to fresh more sulphur-resistant catalysts, such as Pt or metal oxide catalysts [5].

There are many works dealing with the sulphur poisoning of Pd in catalytic oxidations [7,9–12]. So, Hoyos *et al.* [9] studied the influence of the nature of the support on the poisoning of Pd catalysts produced by H_2S. Alumina- and silica-supported Pd catalysts were tested at 350 °C in the oxidation of methane under oxidising conditions (1 vol% CH_4 and 4 vol% O_2 in nitrogen) in the absence and in the presence of 100 ppm H_2S. Both catalysts exhibited sharp deactivation in the presence of sulphur, this deactivation being associated to a decrease of the number active sites. The extent of deactivation was the same for both catalysts, but the rate of deactivation was lower for alumina. This behaviour was

---

*To whom correspondence should be addressed.
E-mail: sordonez@uniovi.es

attributed to the capacity of alumina to trap sulphates and sulphites, as H_2S is fully oxidised to SO_2/SO_3 at the reaction conditions. Yu and Shaw [11] proposed an alternative explanation for the deactivation by sulphur, considering that the formation of surface aluminium sulphates and sulphites plays a key role, decreasing the surface area and trapping active phase in this new structure. Lampert *et al.* [10], compared the poisoning of alumina- and silica-supported catalysts, suggesting that the poisoning is caused by the formation of Pd sulphates, process in which the support plays a key role.

The information about the regeneration of sulphur-poisoned Pd catalysts is much scarcer, in spite of the practical interest of this subject. The first regeneration studies were reported by Hoyos *et al.* [9], who compared the regeneration of a Pd/Al_2O_3 and Pd/SiO_2 sulphur-poisoned catalyst, using nitrogen and hydrogen. They found that the catalyst was regenerated with nitrogen at temperatures higher than 350 °C, whereas in the case of treatment with hydrogen, the activity recovery was lower than 25%. The authors related this effect to the formation of Pd sulphides under reductive conditions, which can be re-oxidised at working conditions. By contrast, Lampert *et al.* [13] found that a sulphur-poisoned PdO/Al_2O_3 catalyst recovered its initial activity after treatment with hydrogen, although the authors do not give details on the deactivation and regeneration conditions. This apparent discrepancy could be explained considering, as pointed out by Yu and Shaw [11], that the support plays a key role in the deactivation process, which, as mentioned previously, is caused mainly by the formation of surface Pd sulphites or sulphates. Whereas silica does not react with sulphur oxides, alumina does, acting then as sulphur sink. On the other hand, as indicated previously, alumina can also react with Pd sulphites and sulphates [10]. This aspect will be discussed in detail latter.

Two recent papers [14,15] deal in part with the regeneration of Pd catalysts under reductive conditions, but they provide limited information, i.e., they do not supply data about the deactivation conditions. So, Limousy *et al.* [14] studied the reduction with hydrogen of surface sulphates in a sulphur-poisoned de-NO_x catalyst (other reducing agents, such as CO where discarded), mentioning the formation of sulphites and sulphides during the reduction. Jones *et al.* [15] compared the regenerability of sulphur-poisoned Pd, Rh and Pt catalysts under hydrogen atmosphere, concluding that this procedure is efficient for Rh, and in minor extension for Pd, whereas it is not efficient for Pt.

Another possibility for regeneration addressed in the literature is treatment with wet gases. This treatment was found to be useful for the regeneration of sulphur-poisoned catalysts, such as Ni catalysts [16] or perovskites [17].

Those studies give only partial information, and, as far as we know, there is not a systematic comparison between the different regeneration alternatives studied in the literature. Therefore, the scope of this work is to carry out an in-depth systematic study of four different procedures for the regeneration of a Pd on alumina catalyst deactivated in the presence of sulphur dioxide: treatment with hydrogen, nitrogen, dry air and wet air, and under vacuum. The influence of the temperatures at which, both deactivation and the regeneration are carried out, is also considered.

2. Experimental

2.1. Materials

A commercial 0.5% (w/w) Pd on alumina catalyst (BASF RO-25) was employed in this work. This catalyst is mesoporous, with surface area 108.5 m^2/g, pore volume 0.4 cm^3/g, and average pore diameter 15.5 nm. Metal dispersion, determined by pulse-chemisorption of hydrogen, was 75.2%. The catalyst, available in extrusions, was milled and crushed, and the fraction between 100 and 250 μm was selected for the reaction studies.

The reactor feeds were made up by mixing adequate proportions of synthetic air, 2.5 vol% methane in synthetic air, and 370 ppmV sulphur dioxide in synthetic air, all supplied by Air Products. Sulphur dioxide was selected as representative of sulphur catalyst poisons, as it is present in many streams of interest, such emissions from carbochemical or petrochemical plants. Besides this, in oxidising conditions, hydrogen sulphide and other sulphur-containing compounds, such as mercaptanes (often encountered in emission from composting facilities, wastewater treatment plants or food processing factories), are transformed into sulphur dioxide, causing poisoning effects similar to those of sulphur dioxide [4].

Gases used in gas chromatography (air, helium and hydrogen) and in temperature-programmed studies (10 vol% H_2 in Ar, 5 vol% O_2 in He, He) were provided by Air Products with purity higher than 99.9995%.

2.2. Reaction studies

The reactor, a lab-scale fixed bed, consisted of a stainless steel tube of 40 cm length and 0.9 cm internal diameter, placed inside an electrical furnace. Five thermocouples measured the reactor wall external temperature at different heights. Temperature in the reaction zone was measured by a thermocouple inserted in the reactor, which provided the control signal to the reactor temperature controller. Reactor feed flow rates were controlled by mass flow regulators supplied by Brooks (5850 TR/DA1B6 Dl, 5850 TR/DB1B3D1 provided with electric unit 0152) and by Bronkhorst HI-TEC (F-201C-FA-22 provided with electric unit E-7100). A dumping vessel avoided possible fluctuations in the reactor inlet stream. Additionally, the system was provided with a relief valve and a manometer.

The catalyst (0.15 g with 100–250 μm diameter), diluted with 1 g of inert glass particles (sieved to 350–500 μm diameter), was loaded in the middle section of the reactor, supported on a metallic mesh. The upper part of the reactor was filled with 355–500 μm glass particles, in order to pre-heat the reaction mixture. The lower part of the reactor remained empty, to limit the pressure drop through the reactor, In this way, the reactor was operated at nearly atmospheric pressure (ΔP = 0.03–0.05 MPa). The reactor feed consisted of 1 L/min (s.t.p.) of synthetic air containing 5000 ppmV methane and, in some experiments, 65 ppmV SO_2. The resulting space-time is 672 g-catalyst min (mol methane)$^{-1}$.

The experimental procedure for producing sulphur-deactivated catalyst samples consisted of circulating through the reactor air–methane mixture, with no SO_2 added, at the selected temperature, for 1 h. It was observed that, following this procedure, the catalyst reached constant activity (constant methane conversion) at the end of this period, this observation is in a good agreement with the reported in other works of our group working at similar conditions with palladium catalysts [4,5,18]. Methane conversion data corresponding to this period of constant activity (just before starting feeding sulphur dioxide), were used as a reference to calculate the activity of the catalyst, defined as the ratio between the methane conversion at a given time on stream and conditions, and the methane conversion corresponding to this reference point. After this 1 h starting period, SO_2 was added to the reaction feed, and the experiment proceeded for another 23 h. Then, the reactor was cooled to room temperature *in situ* by flowing N_2. Temperature for these experiments was fixed in the range 350–550 °C, in order to produce fast loss of catalytic activity. Methane (both in the reactor feed and outlet streams) was analysed on-line by gas chromatography in a Hewlett–Packard 5890A apparatus, equipped with FID and TCD detectors. A mixture of 1.25% CH_4, 1.25% CO_2 and 2% CO by volume and balanced in synthetic air, was used for calibration.

The conditions for producing the aforementioned deactivated catalyst samples, were fixed considering former results [18], in which it was observed that the residual activity of the catalyst used, treated at conditions similar to the ones in this work, does not depend on the sulphur concentration in the feed in the range 15–65 ppmV. It was also observed that a steady-state residual activity was reached after 4–5 h on stream, and that the residual activity depends strongly on reaction temperature [18].

The experiments for regenerating the catalyst samples deactivated according to the aforementioned method were conduced in the same reactor. The procedure (except in the case of regeneration under vacuum), consisted of circulating the selected gas (hydrogen, nitrogen or air) through the reactor during 3 h. In the case of regeneration with air (wet or dry), 5000 ppmV methane were added to the reaction feed, in order to monitor the regeneration process by measuring the evolution of methane conversion with time (in a previous work [4] it was observed that the presence of methane and its combustion products has negligible effect on the regeneration of the catalyst). In the case of regeneration with wet air, the regenerating stream (20,000 ppmV of water in synthetic air), was obtained by pumping the adequate amount of distilled water in the air stream using a syringe pump. In the case of regeneration under vacuum, the catalyst was removed from the reactor, and poured in an electrically heated glass flask connected to a vacuum pump (Baltzers), until an absolute pressure of 130 Pa was attained. The catalyst was then returned to the reactor.

Once the catalyst samples were regenerated, the efficiency of the regeneration processes was characterised by feeding to the reactor, heated at 500 °C, 1 L/min (s.t.p.) of 5000 ppmV methane in air with no SO_2 added, for 25 h, and measuring methane conversion.

2.3. Analysis and catalyst characterisation

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. Powder X-ray diffraction patterns were obtained with a D-5000 Siemens diffractometer, using nickel-filtered CuK_α 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. X-ray photospectroscopy (XPS) spectra were recorded using a SSX-100 ESCA spectrometer with a $MgK\alpha$ source ($h\nu$ = 1253.6 eV). The binding energy of C_{1s} for C at 284.6 eV was used as the reference for the binding energy calibration.

Temperature-programmed desorption (TPD), reduction (TPR) and oxidation (TPO) were carried out in a Micromeritics TPD/TPR 2900 apparatus connected to a MS detector (Gaslab-300). Samples of 10 mg of catalysts were heated from 50 to 1000 °C at 10 °C/min in a flow of 0.1 L/min of different streams:

- TPR experiments: A mixture of 10% H_2 in Ar was used as carrier gas. These experiments simulate the regeneration at reductive conditions (with hydrogen). In this case, the evolution with temperature of H_2, H_2S, SO_2 and CH_4 was recorded.
- TPO experiments: A mixture of 10% O_2 in He was used as carrier gas. These experiments simulate the phenomena taking place during the regeneration at oxidant conditions (with air). The mass signals recorded were CO_2, CH_4, O_2, SO_2, and SO_3.
- TPD experiments: Pure He was used as carrier gas. These experiments simulate the phenomena taking place during the regeneration with inert atmosphere

(with nitrogen). The mass signals recorded were CO_2, CH_4, O_2, SO_2 and SO_3.

It must be noted that a quantitative interpretation of the recorded TP-patterns is not possible because of the low sulphur content of the catalysts.

3. Results and discussion

3.1. Comparison of regeneration procedures

As mentioned previously, partially deactivated catalyst samples were produced by flowing through the reactor SO_2 and methane in synthetic air during 23 h at 350 and 550 °C. Data on the decrease of methane conversion with time on stream observed in these conditions are given in figure 1. It was observed that higher reaction temperature leads to higher residual methane conversion – final methane conversions 1% and 15% at 350 and 550 °C, respectively.

The deactivated catalyst samples were characterised using XRD, XPS and BET analysis. Neither crystallographic changes (both fresh and aged samples showed the same XRD peaks, corresponding to γ-alumina) nor substantial textural (surface area and pore size distribution) differences between fresh and deactivated catalysts were found. Concerning to the XPS analysis, it was observed that, after deactivation, the binding energy of Pd 3d5/2 was displaced 0.2 eV (for both the catalyst deactivated 350 and 550 °C) to higher values with respect to the fresh sample. Although this displacement is attributed to the formation of Pd salts, it is not possible to discriminate between sulphates and sulphites using this technique [19], especially taking into account the low concentration of these species present in the samples. Although XPS analysis also allows to determine the sulphur surface concentration, the obtained values were too low (around 0.5%), being not possible to discriminate differences in the sulphur contents of the catalysts deactivated at different temperatures.

The deactivated catalysts were regenerated under different atmospheres at constant temperature, in the range 350–550 °C, during 3 h, according to the procedures outlined in the experimental section.

Activity recovery is defined as the ratio between the methane conversion attained with the regenerated catalyst at given conditions and time, and the conversion attained with the fresh catalysts defined previously as reference (working in absence of sulphur compound, and taking 1 h as stabilisation period) at the same temperature. The evolution of the activity recovery with time on stream for the different regeneration procedures studied is compared in figure 2 (catalysts deactivated at 350 °C and regenerated at 550 °C) and figure 3 (catalysts deactivated at 550 °C and regenerated at 550 °C), and the main results are summarised in table 1 (reported data correspond to the final steady state conversion obtained). It can be observed that for low regeneration temperature, the regeneration is very inefficient. That is why most of the further experiments were performed at high regeneration temperature.

In most of the cases, it was observed a slight recovery of the catalyst activity after the methane–air mixture was fed to the reactor. This behaviour is assumed to be caused by the conditioning of the active phase, specially when the regeneration is carried out without oxygen. So, in the literature is fully accepted [4,20,21] that the palladium is active for methane oxidation in the form of palladium oxide, the proportion of this specie being marked by the temperature, the oxygen partial pressure and the presence of other reductants.

Results indicate that treatment with hydrogen is significantly the most efficient in all cases, followed by treatment with wet air. Treatment with dry and wet air give similar results for the catalyst deactivated at 350 °C

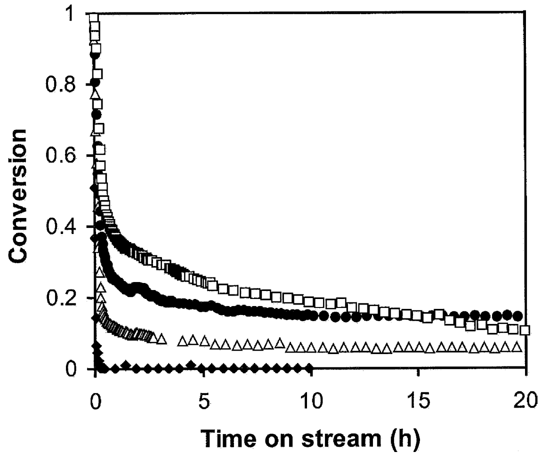

Figure 1. Evolution of methane conversion with time on stream in presence of 65 ppm SO_2 at different temperatures: 350 °C (◆), 450 °C (△), 500 °C (●), and 550 °C (□).

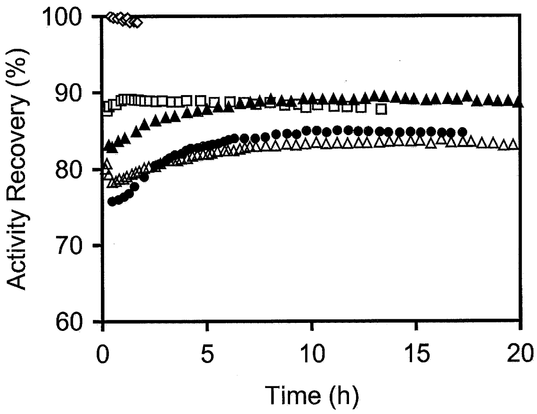

Figure 2. Influence of regeneration atmosphere for the catalyst deactivated at 350 °C and regenerated at 550 °C. Atmospheres tested: hydrogen (◇), dry air (▲), wet air (□), nitrogen (△), and vacuum (●).

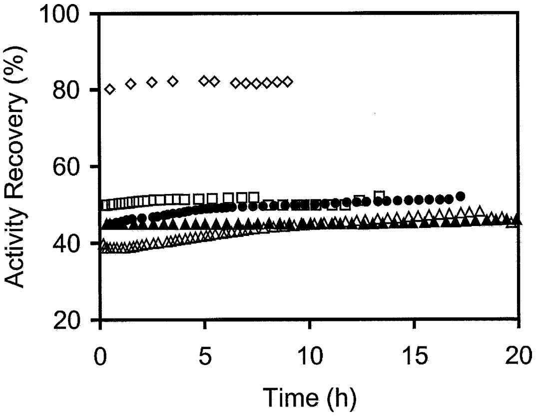

Figure 3. Influence of regeneration atmosphere for the catalyst deactivated and regenerated at 550 °C. For symbols, see figure 2.

and regenerated at 550 °C, whereas for the catalysts deactivated and regenerated at 350 °C, and deactivated and regenerated at 550 °C, regeneration with dry air is less efficient. Regeneration with nitrogen and vacuum offer the worst results.

Regarding the effect of the deactivation temperature, the samples treated in presence of SO_2 at 350 °C show stronger deactivation, but markedly higher regeneration efficiencies than the samples deactivated at 550 °C. Then, Pd–alumina at relatively low temperature (350 °C) is strongly deactivated by SO_2, but it can be easily regenerated. This result is important from a practical point of view for catalytic combustors that can suffer occasional presence of sulphur compounds (i.e., installations for the treatment of off-gases containing VOCs and sulphur compounds that implement sulphur-removal devices upstream the catalytic reactor). In this case, an accidental leak of sulphur compound to the reactor would cause a decrease in the catalytic activity, which could be easily recovered if the catalytic process operates at low temperature.

3.1. *Influence of deactivation temperature for regeneration in air*

Results in the previous section indicate that, although treatment with hydrogen is the most efficient regeneration procedure studied, regeneration with air can be quite efficient, depending on the deactivation and regeneration conditions. Since regeneration with air is, from a practical point of view, much easier and cheaper than regeneration with hydrogen, subsequent experiments were devoted to study the regeneration with air more in depth, specifically the effect of deactivation temperature. For this purpose, deactivated catalyst samples were produced by treatment with SO_2 at different temperatures, in the range 350–550 °C, according to the procedure outlined before. Then, the catalysts were regenerated at 500 °C by passing through the catalysts at air containing 5000 ppm methane, and the evolution of methane conversion with time was recorded.

In order to compare the effect of sulphur dioxide in the deactivation–regeneration process with the deactivation caused by thermal ageing of the catalysts, an additional run was carried out at the same conditions (5000 ppm of methane in air at 550 °C, after a pre-run of 23 h on stream, i.e., with the same time on stream that the poisoned catalysts), with no sulphur dioxide added.

Results obtained (figure 4) show that the catalyst that was not exposed to sulphur-poisoning presents a certain degree of deactivation, while catalysts deactivated in the presence of sulphur dioxide at low temperature (350–450 °C) reach after the regeneration procedure performance only slightly lower. The slight difference between the sample treated in absence of sulphur and the samples treated in the presence of sulphur dioxide can be due both by trapped sulphur (either adsorbed or as sulphites/sulphates) or by agglomeration of crystallites during the deactivation–regeneration process. Since, to the best of our knowledge, there is not experimental evidence on the effect of sulphur compounds on crystalline migration or sintering for Pd, we consider the first possibility more plausible.

At temperatures higher than 450 °C, the regeneration efficiency decreases as the deactivation temperature increases. This suggests that the interaction of sulphur with the active phase is stronger at high temperatures.

According to Yu and Shaw [11], the sulphur poisoning of Pd catalysts proceeds through two consecutive steps: adsorption of SO_2 and reaction of the adsorbed SO_2 to form Pd sulphites or sulphates, depending on the

Table 1

Regeneration efficiency (%) for different regeneration procedures for the catalysts deactivated at 350 and 550 °C

Procedure	Catalyst deactivated at 350 °C			Catalyst deactivated at 550 °C	
	$T_{reg} = 350°C$	$T_{reg} = 450°C$	$T_{reg} = 550°C$	$T_{reg} = 450°C$	$T_{reg} = 550°C$
Dry air	12	38	88	13	46
Wet air (2% H_2O)	15		87		52
Nitrogen	9		81		45
Vacuum	11		83		52
Hydrogen	55		99		82

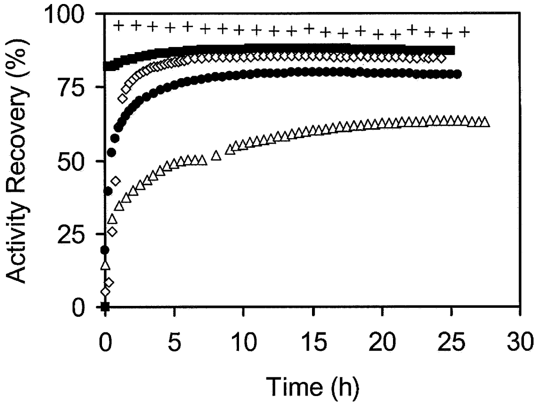

Figure 4. Activity recovery for catalysts deactivated at different temperatures. Regeneration carried out in air with 5000 ppmV methane at 550 °C. Catalysts deactivated at 350 °C (■), 450 °C (◇), 500 °C (●), and 550 °C (△). Self-deactivation pattern of the catalyst used for the oxidation of 5000 ppm of CH_4 in absence of SO_2 at 550 °C is also provided (+).

concentration of O_2 in the medium. The adsorption is an equilibrium exothermic process, disfavoured at high temperature. On the other hand, the second step is a chemical reaction, in which reaction rate increases as temperature increases. This mechanism would explain the increase of the degree of deactivation observed at low temperature (low temperature favours the adsorption of sulphur dioxide), and the higher degree of irreversibility of the process observed at high temperature (high temperature would favour the formation of Pd sulphites or sulphates from adsorbed sulphur dioxide).

3.2. Temperature-programmed experiments

In order to get a better understanding of the phenomena taking place during the regeneration procedures studied, different temperature-programmed experiments were carried out, according to the procedure outlined in the experimental section, with the catalysts poisoned at 350 and 550 °C. The phenomena taking place on the catalysts during the TPO, TPR and TPD, can be considered as similar to those taking place during the regeneration with air, hydrogen and nitrogen, respectively. So, although the concentration of O_2 and H_2 in TP experiments is lower than the one corresponding to the regeneration, in both experiments the amounts of the reactive gases are much larger than that needed for complete the reaction of the sulphur compounds.

In the case of TPR (figure 5), the main sulphur compound released was hydrogen sulphide, although a small release of SO_2 was also observed for the catalyst deactivated at 350 °C. However in the case of TPO (figure 6) and TPD (figure 7) the only sulphur product evolved was SO_2. Neither methane nor carbon oxidation products (CO or CO_2) were detected. This fact is in a good agreement with findings of other authors [22], who stated that the adsorption of methane on Pd is very weak. Concerning to the TPD experiments, in the case of the catalyst deactivated at 350 °C, the only species evolved was SO_2, no oxygen release being observed, while in the case of the catalyst deactivated at 550 °C, a slight oxygen release was observed at temperature slightly lower than that of the SO_2 release.

Regarding to the uptakes, TPR experiments showed strong hydrogen uptakes, associated to the release of H_2S. In the case of TPO experiments, a peak of O_2 uptake was observed, displaced at higher temperature that the peak corresponding to SO_2 release.

The complex results of the temperature-programmed experiments could be explained by the participation of the support in the processes and the presence of sulphites and sulphates. Concerning to the participation of the support, Lampert *et al.* [10] suggested that supports able to form sulphates, as Al_2O_3, can participate in the regeneration of the catalyst. So, the following reactions could take place in sulphur-poisoned Pd/Al_2O_3, depending on the nature of sulphur compound present (sulphite or sulphate):

$$PdSO_3 \rightarrow PdO + SO_2 \quad (1)$$

$$PdSO_4 \rightarrow PdO + SO_2 + O_2 \quad (2)$$

$$3PdSO_3 + 1.5O_2 + Al_2O_3 \rightarrow Al_2(SO_4)_3 + 3PdO \quad (3)$$

$$3PdSO_3 + Al_2O_3 \rightarrow Al_2(SO_3)_3 + 3PdO \quad (4)$$

$$3PdSO_4 + Al_2O_3 \rightarrow Al_2(SO_4)_3 + 3PdO \quad (5)$$

$$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_2 + O_2 \quad (6)$$

$$Al_2(SO_3)_3 \rightarrow Al_2O_3 + 3SO_2 \quad (7)$$

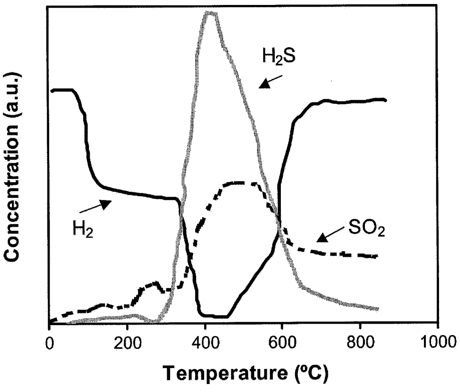

Figure 5. Temperature-programmed reduction patterns for the catalyst deactivated at 350 °C.

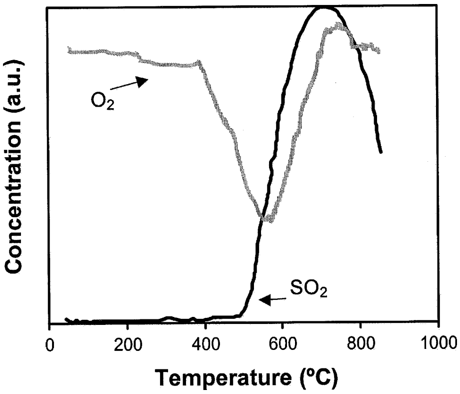

Figure 6. Temperature-programmed oxidation patterns for the catalyst deactivated at 350 °C.

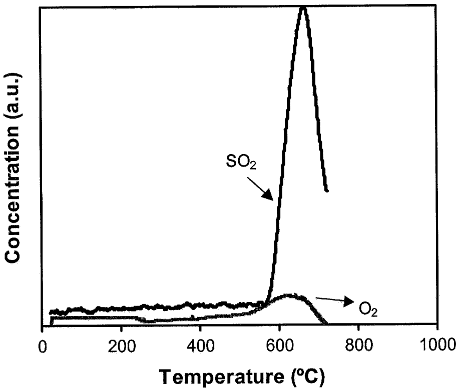

Figure 7. Temperature-programmed desorption patterns for the catalyst deactivated at 550 °C.

These mechanisms were proposed by Yu and Shaw [11] for alumina supported catalysts poisoned with 250 ppm H_2S, and by Luo *et al.* [23] for the reaction of 1% SO_2 in air with ceria-supported Pd catalysts.

The null or very small release of oxygen observed in TPD experiments, would indicate that the SO_2 release would be produced by the decomposition of Pd sulphite [reactions (1) or (4 + 7)], since the release of SO_2 from Pd sulphate is accompanied by the release of oxygen. The oxygen uptakes observed in TPO experiments, which can be attributed to reactions (1) and (3), lead to the same conclusion. On the other hand, the catalyst deactivated at 550 °C (condition at which regeneration is less efficient) showed a higher oxygen release, which would be related to a higher content on Pd sulphate in this sample. This suggests a relation between the difficulty of regeneration and the content of Pd sulphate, sulphate being more difficult to regenerate than sulphite, and the formation of sulphate versus sulphite being favoured at high temperature.

The higher efficiency of the regeneration with air, if compared with regeneration with nitrogen, could be caused by a more efficient regeneration of Pd sulphite in presence of oxygen [reaction (3) takes place in addition to reaction (1)].

It is also observed that the sulphur release takes place at lower temperatures in the TPR experiments than in TPD and TPO experiments, which is in a good agreement with the lower temperatures needed for the regeneration of the catalyst by means of treatment with H_2.

4. Conclusions

Among the five different procedures (treatments with hydrogen, vacuum, nitrogen, wet air and dry air) tested for the regeneration of an alumina-supported Pd catalyst, deactivated by SO_2, the most efficient was treatment with hydrogen, followed by treatment with air. Samples deactivated at low temperature showed stronger deactivation, but were easier to regenerate. The efficiency of the regeneration increased also as the regeneration temperature increased.

Characterisation of the poisoned catalysts using TPR, TPD and TPO suggests that Pd sulphite is easier to regenerate under inert or oxidant conditions, and that the formation of this compound is favoured at low temperature.

Acknowledgments

This work has been supported by a grant of the Regional Asturian Government (Contract PC-CIS01–30) and COGERSA. The catalyst has been kindly supplied by BASF-Spain. XPS experiments have been carried out at the Unité de Catalyse, Université Catholique de Louvain, Louvain La Neuve, Belgium. The authors wish to acknowledge Prof. Bernard Dehmon and Dr. Mihai Alifanti for their help in these experiments and their fruitful discussions, and Eva Díaz for her cooperation.

References

[1] N. Mukhopadhyay and E.C. Moretti, *Reducing and Controlling Volatile Organic Compounds* (Centre for Waste Reduction Technologies-AIChE, New York, 1993).
[2] R.E. Heyes and S.T. Kolazkowski, *Introduction to Catalytic Combustion* (Gordon and Breach Sci. Pub., Amsterdam, 1997).
[3] S.H. Schneider, *Global Warming* (Vintage Books, New York, 1989).
[4] P. Hurtado, S. Ordóñez, H. Sastre and F.V. Díez, Appl. Catal. B 47 (2004) 85.
[5] P. Hurtado, S. Ordóñez, H. Sastre and F.V. Díez, Chemosphere 55 (2004) 681.
[6] M. Waqif, J. Bachelier, O. Saur and J.C. Lavalley, J. Mol. Catal. 72 (1992) 127.

[7] P. Gélin and M. Primet, Appl. Catal. B 39 (2002) 1.

[8] V. Maeyoo, D.L. Trimm and N.W. Cant, Appl. Catal. B 16 (1998) 105.

[9] L.J. Hoyos, H. Praliaud and M. Primet, Appl. Catal. A 98 (1993) 125.

[10] J.K. Lampert, M.S. Kazi and R.J. Ferrauto, Appl. Catal. B 14 (1997) 211.

[11] T. Yu and H. Shaw, Appl. Catal. B 18 (1998) 105.

[12] D.L. Mowery, M.S. Graboski, T.R. Ohno and R.L. McCormick, Appl. Catal. 21 (1999) 157.

[13] J.K. Lampert, M.S. Kazi and R.J. Ferrauto, SAE 961971 (1996).

[14] L. Limousy, H. Mazhoul, J.F. Brilhac, F. Garin, G. Marie and P. Gilot, Appl. Catal. B 45 (2003) 169.

[15] J.M. Jones, V.A. Dupont, R. Brydson, D.J. Fullerton, N.S. Nasri, A.B. Ross and A.V.K. Westwood, Catal. Today 81 (2003) 589.

[16] J.R. Rostrap-Nielsen, J. Catal. 21 (1971) 171.

[17] I. Rosso, E. Garrone, F. Geobaldo, B. Onida, G. Saracco and V. Specchia, Appl. Catal. B 30 (2001) 61.

[18] S. Ordóñez, P. Hurtado, H. Sastre and F.V. Díez, Appl. Catal. A 259 (2004) 41.

[19] C.D. Wagner, W.M. Riggs, L.E. Dayis, J.F. Moulder and G.E. Muilemberg, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin Elmer Corp., Eden Prairie MI, 1979).

[20] Y.H. Chin and D.E. Resasco, in: *Catalysis*, Vol. 14, J.J. Spivey, ed. (The Royal Society of Chemistry, London, 1999), 3.

[21] D. Ciuparu, D.M. Lyubowsky, E. Altman, L.D. Pfefferle and A. Datye, Catal. Rev. 44(4) (2002) 593.

[22] E.M. Cordi and J.L. Falconer, J. Catal. 162 (1996) 104.

[23] T. Luo, J.M. Vohs and R.J. Gorte, J. Catal. 210 (2002) 397.