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Complete oxidation of methane at low temperature over Pt and Pd catalysts for the abatement of lean-burn natural gas fuelled vehicles emissions: influence of water and sulphur containing compounds

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Abstract

The catalytic activity of fresh Pd and Pt catalysts supported on γ-alumina in the complete oxidation of CH_4 traces under lean-burn conditions was studied in the presence or the absence of water or H_2S. Steam-aged catalysts were also studied in order to simulate long-term ageing in real lean-burn natural gas fuelled vehicles (NGVs) exhaust conditions. Without water or H_2S added to the feed, Pd catalysts exhibit a superior catalytic activity in methane oxidation compared to Pt ones, whatever the catalysts were fresh or aged. The addition of 10 vol.% water vapour to the feed strongly affects the activity of the fresh Pd catalyst, thus being only slightly more efficient than the fresh Pt one. H_2S has a strong poisoning effect on the catalytic activity of Pd catalysts, while Pt catalysts are more resistant. The fresh H_2S-poisoned Pd/Al_2O_3 catalyst was studied by TPD in O_2/He. Poisoning species decompose above 873 K as SO_2 and O_2 in relative concentrations consistent with the decomposition of surface sulphate species. However, a treatment in O_2/He at temperatures as high as 923 K does not allow the complete regeneration of the catalytic activity of H_2S-poisoned Pd/Al_2O_3. A mechanism involving the poisoning of PdO by sulphate species is proposed. Different diffusion processes by which these sulphate species can migrate back and forth between PdO and the support, depending on the experimental conditions, are suggested.

Keywords: Methane oxidation; Catalytic combustion; Palladium; Platinum; Al_2O_3; Catalytic activity; Water inhibition; Poisoning by sulphur

1. Introduction

Natural gas fuelled vehicles (NGVs) appear attractive to solve transportation problems in cities and reduce pollution since, compared to diesel, NGV engines produce less NO_x and particulates. As a matter of fact, NGV programs are currently developing very rapidly in European countries, and especially in France for buses. Natural gas engines can operate under lean conditions so that the fuel efficiency can be much increased compared to stoichiometric conditions. Under these conditions, unburned methane, a potent greenhouse gas, is emitted in the exhaust gases. In Europe, the Euro III standard (implemented from October 2000) defines a limit value, for CH_4 emissions from heavy-duty NGVs, equal to 1.6 g kWh^{-1}

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during a transient cycle test protocol (ETC). In order to meet this severe regulation, a catalytic exhaust converter is necessarily installed on lean-burn heavy-duty NGVs sold for the European market. This device is designed to achieve methane emission abatement by catalytic combustion.

The approach raises several difficulties because of the high stability of the methane molecule together with specific reaction conditions: (i) low temperatures at which the catalyst must operate, typically less than 500–550 °C, (ii) low concentrations of methane (500–1000 ppm), (iii) large amounts of water vapour (10–15%) and CO_2 (15%), (iv) large excess of oxygen, and (v) presence of SO_x (about 1 ppm) and NO_x. Unlike catalytic combustion which requires the design of catalytic materials able to withstand high temperatures in atmospheres containing steam and oxygen, it is clear that the thermal stability of the catalyst is out of concern. The main objective is rather to design catalytic materials exhibiting the highest activity at the lowest temperature and the best resistance to poisons present in the exhaust gases. Noble metal catalysts (especially palladium and to a lesser extent platinum) supported on oxide carriers appeared as the best catalysts and their properties in the complete oxidation of methane at low temperature were extensively studied so far [1,2].

Although being the most active, Pd catalysts exhibit a strong sensitivity to water and sulphur containing compounds, which represents serious drawbacks to their use for NGVs exhaust after treatment [1]. Water was shown to act as a strong inhibitor on the catalytic activity in methane oxidation, by competing with methane for adsorption on catalytic sites [3–7]. In addition, water would induce a slow irreversible deactivation of Pd/Al_2O_3 possibly due to the progressive transformation of surface PdO active sites into $Pd(OH)_2$ less active sites [3,7]. Sulphur containing compounds were shown to readily convert into SO_x and strongly adsorb at the surface of PdO particles as stable sulphate species, therefore decreasing the number of active sites until saturation of the active sites surface by sulphate species and complete loss of catalytic activity for methane oxidation [8–13]. The support was observed to influence the rate of poisoning of the PdO catalyst, being rapid on a non-sulphating support like SiO_2 and much slower on a sulphating one like Al_2O_3 [8,9]. Water could also increase the deactivation rate of Pd/Al_2O_3 catalysts for reaction temperatures of at least 793 K [11,12]. Much fewer studies were devoted to Pt catalysts. It was shown that Pt would be more resistant to sulphur poisoning [8].

The aim of the present study is to investigate the catalytic properties of Pd and Pt catalysts supported on γ-alumina in the complete oxidation of methane traces under lean conditions at low temperature. The influence of water and H_2S added separately to the reaction mixture on the catalytic activity was also examined. Poisoned Pd catalysts were studied by FTIR spectroscopy and temperature programmed desorption experiments in oxygen/helium stream in order to determine the nature and the thermal stability of the poisoning species. Further understanding of the mechanism leading to the poisoning of alumina-supported Pd catalysts by sulphur containing compounds is obtained. Although the study is devoted to a better understanding of catalysts for methane combustion in lean-burn NGV exhausts, the results may be also useful for applications in which methane combustion is performed at low temperature.

2. Experimental

2.1. Catalysts preparation

2.20 wt.% Pd (respectively, 1.92 wt.% Pt) catalysts were prepared by impregnation of crushed γ-Al_2O_3 (Rhodia SPH 569, specific surface area of 136 $m^2\,g^{-1}$, pore volume of 2.83 $cm^3\,g^{-1}$, containing less than 0.015 wt.% Cl) with $Pd(NH_3)_4(NO_3)_2$ (respectively, $Pt(NH_3)_4(NO_3)_2$) aqueous solution, the suspension being maintained under stirring at 333 K for 1 h. After complete removal of water by evaporation under reduced pressure, the catalysts were dried overnight in air at 120 °C and calcined in air at 773 K for 4 h. The as-prepared catalysts are labelled as *fresh* catalysts.

In order to simulate long-term ageing in lean-burn exhaust conditions, the so called *aged* catalysts were obtained by treatment of the *fresh* (oxidised) catalysts in a 10 vol.% H_2O–10% O_2–N_2 mixture for 24 h at 873 K and purge in nitrogen before cooling. No loss of noble metal was observed after this treatment, as shown by chemical analysis measurements.

2.2. Catalytic activity studies

Catalytic tests were carried out using a U-shaped quartz reactor with a inner diameter of 16 mm and a quartz frit to support the catalyst (200 mg). The reactor was operated in down flow and the temperature measured at the frit was taken as the reaction temperature. The standard test stream was a model reaction mixture containing 2000 vol. ppm CH_4 and 5 vol.% O_2, balance helium. The total flow rate was 6.5 l h^{-1} (GHSV $= 20\,000\,h^{-1}$). For experiments under wet conditions, 10 vol.% water vapour was added to the standard feed by injection of liquid water in a syringe at a controlled rate. For experiments in the presence of H_2S, the 5 vol.% CH_4/He mixture used to obtain the standard feed was substituted by a 5 vol.% CH_4/2480 vol. ppm H_2S/He mixture, so as to obtain 2000 vol. ppm CH_4/100 vol. ppm H_2S, 5 vol.% O_2 in helium.

Different types of catalytic tests were performed. When the methane conversion was measured as a function of the temperature, the reaction temperature was varied from 423 K up to the temperature at which 100% CH_4 conversion was reached by applying successive heating ramps of 50 K (heating rate of 1 K min^{-1}) with intermediate heating of 1 h at each final temperature. Prior to the catalytic testing, the catalysts were treated as follows: (i) *fresh* (oxidised) catalysts: in O_2 at 773 K for 1 h and in He during cooling to 423 K; (ii) *aged* catalysts: in 5 vol.% O_2–He at 873 K for 1 h and in He during cooling to 423 K. For experiments with H_2O or H_2S, isothermal tests consisting of measuring the catalytic activity as a function of time on stream, at the temperature of 50% CH_4 conversion (T_{50}) in the standard feed, were performed. Then H_2O or H_2S was suppressed from the feed and the activity measured for several additional hours in order to study the catalyst regeneration. Prior to isothermal tests, the catalyst was pre-treated and tested under standard feed until reaching T_{50} following the same procedure as used for conversion versus temperature tests.

The CH_4, CO_2, H_2S and SO_2 concentrations at the outlet of the reactor were determined using a Hewlett-Packard MTI M200 micro-chromatograph equipped with two TCD detection units (one having a Poraplot-U column, one having a Molecular Sieve A column). CO never formed under reaction conditions. CH_4 conversion was calculated according to the equation: $[CO_2]/([CO_2]+[CH_4])$, $[CO_2]$ and $[CH_4]$ being the concentrations of CO_2 and CH_4, respectively, at the reactor outlet.

2.3. Catalysts characterisation

Specific surface areas of the catalysts samples were measured with nitrogen using a home-made apparatus. XRD patterns were obtained using Cu Kα radiation on a Philips PW1710 diffractometer.

The catalysts dispersion was derived from the measurement of the uptake of H_2 chemisorbed at room temperature following the method described by Benson and Boudart [14]. The samples were treated in vacuo at 723 K for 1 h, contacted with ca. 150 Torr H_2 at 573 K, treated in vacuo at 573 K for 1 h and cooled down to room temperature before chemisorption studies. O_2/H_2 titrations were also performed, being in good agreement with H_2 chemisorption. For the calculation of dispersion, adsorption stoichiometries of H_{ads}/M_s and O_{ads}/M_s were assumed to be equal to unity, M_s being a surface metal atom.

Main physico-chemical characteristics of the catalysts are reported in Table 1. The specific surface area decreases from 138 to 120 $m^2\,g^{-1}$ upon steam ageing treatment at 873 K. This slight variation indicates that the alumina is only little affected by the ageing treatment and that eventual changes in the catalytic properties for methane oxidation could not originate from surface transformations of the alumina support.

IR spectroscopy provides a tool to study the sulphate species deposited on the catalysts upon reaction with the H_2S containing feed. The air-contacted samples (35 mg) were pressed into thin wafers, introduced in an IR cell for treatment under vacuum at 573 K for 2 h. The spectra were recorded at room temperature under vacuum with a Nicolet Magna 550 (resolution 4 cm^{-1},

Table 1
Main physico-chemical characteristics of Pt and Pd catalysts

Samples	BET area ($m^2\,g^{-1}$)	Metal content (wt.%)	Dispersion (%)
Fresh Pd/Al_2O_3	137	2.20	16
Aged Pd/Al_2O_3	119	2.20	11
Fresh Pt/Al_2O_3	139	1.92	40
Aged Pt/Al_2O_3	120	1.92	9

32 scans). Al_2O_3 samples with known amounts of sulphate species were also prepared by impregnation of the alumina with H_2SO_4 solutions and analysed. The background spectrum of the alumina was subtracted. For all samples, a sharp band with a maximum at ca. 1390 cm^{-1}, characteristic of surface sulphate vibrations [15], was observed. Its integrated intensity was measured as a function of sulphur content, giving rise to a nice linear correlation between 0 and 1.4 wt.% S. It was derived that the integrated intensity of the 1390 cm^{-1} band was equal to 60 cm^{-1} for 1 wt.% S. This calibration was used to determine the amount of sulphur in catalysts sulphated in H_2S containing feed.

The fresh H_2S-poisoned Pd/Al_2O_3 catalyst was studied by temperature-programmed desorption (TPD) in 600 vol. ppm O_2/He. The experiment was carried out in a U-shaped quartz reactor loaded with 0.03 g catalyst by using a Balzers QMA 125 quadrupole mass spectrometer. The air-contacted-poisoned catalyst was directly heated in O_2/He (from 298 up to 1273 K) at a heating rate of 5 K min^{-1}. The desorbed species were continuously monitored as a function of time/temperature. The mass spectrometer was calibrated for SO_2 and O_2 gases.

3. Results

3.1. Influence of ageing on the catalytic activity in dry feed

The catalytic activities of fresh and aged Pt and Pd catalysts plotted as a function of reaction temperature in the standard dry feed are compared in Fig. 1. Table 2 reports the temperatures at which 10, 30 and 50% CH_4 conversions were reached for these different samples. For fresh catalysts, it can be clearly seen that Pd/Al_2O_3 is much more active than Pt/Al_2O_3, in agreement with previous reports in the literature [3,16–21]. For instance, the T_{50} is increased by more than 100 K for Pt/Al_2O_3 compared to the Pd catalyst. The apparent activation energy value equal to 85 kJ mol^{-1} for both catalysts fairly agrees with values previously reported for other reaction mixture compositions without water except that formed by the reaction [5,6,22].

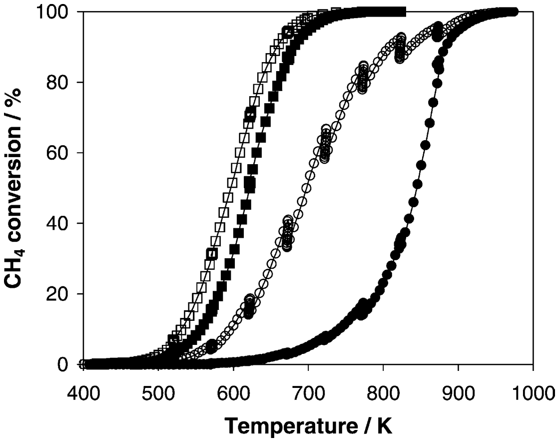

Fig. 1. Methane conversion over fresh (open symbols) and aged (filled symbols) Pd/Al_2O_3 (□, ■) and Pt/Al_2O_3 (○, ●) catalysts vs. temperature in dry feed. Feed composition: 2000 vol. ppm CH_4; 5 vol.% O_2; He balance (200 mg catalyst; total flow rate of 6.5 l h^{-1}; GHSV = 20 000 h^{-1}). At each 50 K increase of the temperature, the conversion was recorded for 1 h.

Interestingly, the fresh Pd catalyst does not exhibit any deactivation at each temperature plateau. This contrasts with previous findings indicating a slow deactivation of Pd/Al_2O_3 with time on stream, the activity being recovered after a purge of the catalyst in helium at 873 K [7]. This deactivation was attributed to the slow formation of inactive (or less active) $Pd(OH)_2$ species at the surface of active PdO

Table 2
Apparent activation energy and temperatures at which 10, 30 and 50% CH_4 conversions were reached for the complete oxidation of methane over Pd and Pt catalysts under standard dry reaction mixture[a]

Catalyst	T_{10} (K)	T_{30} (K)	T_{50} (K)	E_a (kJ mol^{-1})
Fresh Pd/Al_2O_3	531	571	593	85
Aged Pd/Al_2O_3	553 (+22)	593 (+22)	622 (+29)	103
Fresh Pt/Al_2O_3	596	653	698	85
Aged Pt/Al_2O_3	743 (+147)	813 (+160)	843 (+145)	90

[a] The values in parentheses indicate the variation of the temperatures between fresh and aged catalysts.

particles by reaction of surface PdO entities with water formed by the reaction according to the equilibrium: $PdO + H_2O = Pd(OH)_2$ [3,7]. In the present study, the CH_4 partial pressure is five times lower than that used in these studies, which involves water partial pressures at identical conversion 10 times lower in our present experiments. This would result in much weaker formation of $Pd(OH)_2$ and, therefore, in no detectable influence of the water produced by the reaction on the catalytic activity.

On the contrary to fresh Pd/Al_2O_3, fresh Pt/Al_2O_3 exhibits a significant deactivation at each temperature plateau. This result has not yet been mentioned in the literature. Previous studies on the complete oxidation of methane over Pt/Al_2O_3 were performed on catalysts prepared from Cl containing Pt precursors [16,17,23,24]. Cl originating from the metal precursor was shown not to be fully removed upon activation treatments and to strongly inhibit the catalytic activity [23]. It is likely that, in these studies, the increase of activity related to Cl removal during catalytic reaction would compensate for the decrease of the activity due to Pt sintering. In our present experiment, the observed decrease of the activity with time on stream is not yet explained. We observed that Pt dispersion decreased from 40% before catalytic testing to 9% after catalytic testing, which could explain the deactivation, especially in high temperatures region. Further studies are however required to explain the catalytic behaviour of Pt/Al_2O_3.

Steam ageing has little effect on the catalytic activity of Pd/Al_2O_3 while it induces a drastic decrease of the Pt/Al_2O_3 catalytic activity. For Pd/Al_2O_3, the T_{50} increases only by 30 K upon steam ageing while the increase of T_{50} reaches 150 K for Pt/Al_2O_3. This could be related to different resistance of catalysts against sintering upon steam ageing. As shown in Table 1, it can be observed that Pd sintering is moderate, Pd dispersion decreasing from 16% for the fresh sample to 11% for the aged one. On the contrary, the variation is much more pronounced for Pt/Al_2O_3, Pt dispersion decreasing from 40 to 9% upon ageing. This is not surprising if considering that, in the fresh state, the Pt catalyst is much more dispersed than the Pd one.

Table 3
Rates of CH_4 oxidation into CO_2 at 543 K expressed in moles of formed CO_2 per hour and per mole of metal, and turn over rates at 543 K (based on metal dispersion values given in Table 1)

Samples	Reaction rate ($mol\,CO_2\,h^{-1}\,mol^{-1}$ metal)	Turn over rate (h^{-1})
Fresh Pd/Al_2O_3	1.90	11.9
Aged Pd/Al_2O_3	0.85	7.7
Fresh Pt/Al_2O_3	0.57	1.4
Aged Pt/Al_2O_3	0.021[a]	0.23

[a] Calculated from the catalytic activity measured at 652 K by taking into account an apparent activation energy of $90\,kJ\,mol^{-1}$.

Table 3 reports the rates of CO_2 formation at 543 K over the fresh and aged catalysts together with the corresponding turn over rates, in h^{-1}, calculated on the basis of metal dispersion values measured before catalytic testing. On this basis, turn over rates are minimum values since metal sintering can occur during catalytic reaction, particularly for the fresh Pt catalyst. When comparing turn over rates of the fresh catalysts at 543 K, Pd appears approximately 10 times more active than Pt. The difference is even more pronounced with aged catalysts since a factor of 30 between Pd and Pt turn over rates can be deduced. This establishes clearly again the superiority of Pd/Al_2O_3 over Pt/Al_2O_3 for CH_4 combustion. Interestingly, it can be noticed that turn over rates decrease upon ageing, especially in the case of Pt/Al_2O_3 for which the TOR of the aged sample decreases to a value 80% lower than that of the fresh one. This suggests that the decrease of the metal dispersion upon steam ageing is likely not the only factor influencing the catalytic activity decrease.

3.2. Catalytic activity in wet feed

The catalytic activity of Pd/Al_2O_3 and Pt/Al_2O_3 catalysts, in fresh and aged states, was studied as a function of reaction temperature in the standard reaction mixture which 10 vol.% H_2O was added to. The results are reported in Fig. 2. Table 4 reports T_{10}, T_{30} and T_{50} values derived from Fig. 2.

Table 4
Temperatures at which 10, 30 and 50% CH_4 conversions were reached for the complete oxidation of methane over Pd and Pt catalysts under wet reaction mixture

Catalyst	T_{10} (K)	T_{30} (K)	T_{50} (K)
Fresh Pd/Al_2O_3	623	673	698
Aged Pd/Al_2O_3	623	664	693
Fresh Pt/Al_2O_3	633	695	738
Aged Pt/Al_2O_3	753	813	843

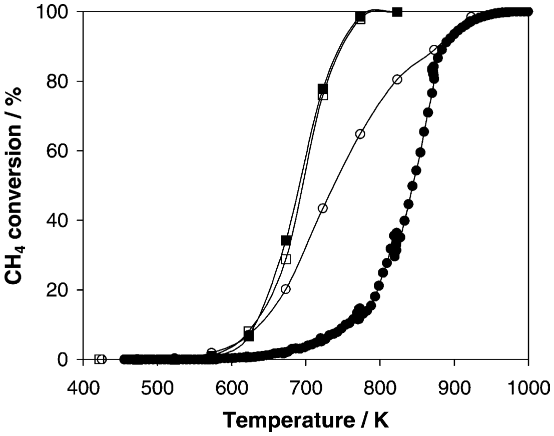

Fig. 2. Methane conversion over fresh (open symbols) and aged (filled symbols) Pd/Al_2O_3 (□, ■) and Pt/Al_2O_3 (○, ●) catalysts vs. temperature in wet feed. Feed composition: 2000 vol. ppm CH_4; 5 vol.% O_2; 10 vol.% H_2O; He balance (200 mg catalyst; total flow rate of 6.5 l h^{-1}; GHSV = 20 000 h^{-1}). At each 50 K increase of the temperature, the conversion was recorded for 1 h.

The addition of 10 vol.% H_2O to the reaction feed has a drastic effect on the catalytic activity of Pd/Al_2O_3 in methane combustion. Approximately 100 K increase of T_{50} is observed for the fresh catalyst when H_2O is added, while this increase is still as high as 70 K for the aged one. Interestingly, fresh and aged Pd catalysts exhibit exactly the same catalytic activity under wet conditions.

For the fresh Pt catalyst, the presence of 10 vol.% H_2O in the feed has a moderate impact on the catalytic activity. The T_{50} increases by 40 K upon H_2O addition. For the aged Pt catalyst, the addition of water has no influence on the catalytic activity. It turns out that the difference of activity observed between fresh Pd and Pt catalysts, large in dry conditions, is much reduced in wet conditions, even though Pd still appears as the best catalyst for methane combustion. This is no longer true for aged catalysts. The aged Pt/Al_2O_3 shows a T_{50} higher by 150 K compared to the aged Pd/Al_2O_3 catalyst, which still makes Pd catalysts as potentially much superior to Pt ones in lean-burn NGV CH_4 abatement.

Fig. 3 shows the evolution of the catalytic activity of Pd and Pt catalysts versus time after addition of 10 vol.% H_2O to the reaction feed, at a given temperature. The temperature of the reaction depended on the studied catalyst: 633 and 643 K for the fresh and aged Pd catalysts, respectively, 738 and 843 K for the fresh and aged Pt catalysts, respectively. The temperatures were chosen so as to follow the activity at approximately 50% CH_4 conversion under wet conditions. For Pd catalysts, 100% conversion is reached in dry conditions. The reaction temperature was then adjusted so as to get 75–80% CH_4 conversion in dry conditions. For each experiment, the first experimental point represents the activity measured in dry feed. Then, 10 vol.% H_2O is added to the feed and the activity recorded versus time for 8–9 h. Water injection was then suppressed and the activity again recorded for 15 additional hours.

Fresh and aged Pd catalysts exhibit exactly the same catalytic behaviour during the experiment. Upon addition of water, the CH_4 conversion immediately decreases from 75 to 80% down to ca. 15%. A further small decrease of CH_4 conversion to ca. 10% can be observed after 9 h exposure to the wet feed. Upon suppression of H_2O supply to the feed, the CH_4 conversion immediately reaches ca. 65% and remains nearly constant until the end of the experiment. The sharp decrease of the catalytic activity of Pd/Al_2O_3 catalysts in methane combustion observed upon addition of water to the reaction mixture is in full agreement with the strong inhibition of water on the Pd activity in CH_4 combustion already reported in the literature [4–6]. The influence of water concentration on the rate of oxidation of Pd/Al_2O_3 was investigated by several groups [4–6]. An apparent negative order, which could vary depending on the experimental conditions between −0.4 and −1, was found. A competition between methane and water for the active sites leading to the formation of $Pd(OH)_2$ at PdO surface sites was proposed [4]. The fact that the catalytic activity is not fully recovered after reaction with the wet feed suggests a slight slow irreversible deactivation due to the presence of water, which is in agreement with a previous study [7] and could be attributed to a slow transformation of the active sites in the presence of large amounts of water.

For the fresh Pt/Al_2O_3 catalyst, the addition of 10 vol.% H_2O to the feed induces the sudden decrease of the CH_4 conversion from 65 to ca. 40%. The activity then slowly decreases further to ca. 30% over a 9 h period in wet stream. The initial activity is recovered upon suppressing water in the feed and a slow significant deactivation with time on stream

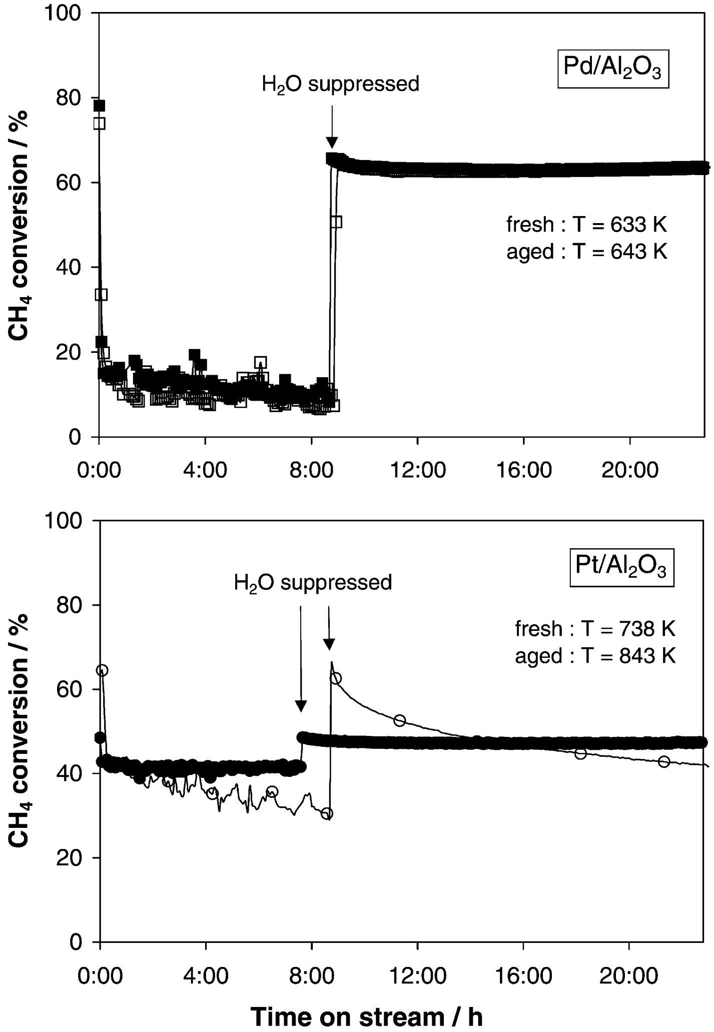

Fig. 3. Influence of 10 vol.% water addition on methane conversion over fresh (open symbols) and aged (filled symbols) Pd/Al_2O_3 (□, ■) and Pt/Al_2O_3 (○, ●) catalysts vs. time on stream. Feed composition: 2000 vol. ppm CH_4; 5 vol.% O_2; He balance (200 mg catalyst; total flow rate of 6.5 l h^{-1}; GHSV = 20 000 h^{-1}). The catalytic activity was measured in dry feed until reaching the temperature corresponding to approximately 50% conversion in wet feed (see Fig. 2). For the most active catalysts, the temperature was adjusted so as not to exceed 80% conversion in dry feed. The first experimental point represents the activity in dry feed. Then H_2O is added to the reaction mixture and the activity measured with time.

can be observed in dry feed. As for the Pd catalyst, the reversible loss of catalytic activity upon water addition can be explained by a competition of water with methane for active sites. The reduced loss of activity compared to Pd suggests a lower inhibition effect by water. This can be partly explained by the higher reaction temperature (738 K for Pt, 633 K for Pd). Burch et al. [4] have shown that the inhibiting effect of water on the catalytic activity of Pd/Al_2O_3 decreased with increasing temperature, becoming small above 723 K. A further argument can be found in the catalytic behaviour of the aged Pt catalyst, at 843 K, i.e. 200 K above the temperature chosen for the experiment with Pd/Al_2O_3. At this temperature, the addition of water produces only a small decrease of the activity (less than 10%), and the full recovery of the activity upon water suppression, which indicates a very small influence of water on the activity.

3.3. Catalytic activity in the presence of H_2S

In order to simulate a long-term exposure of the catalysts to sulphur containing compounds present at very low concentrations (about 1 ppm) in natural gas, the catalysts were exposed to a dry reaction mixture containing 100 vol. ppm H_2S. The catalysts were heated in the dry sulphur-free reaction mixture until the temperature at which 50% CH_4 conversion is obtained. The temperatures were 523, 623, 698 and 843 K for fresh Pd/Al_2O_3, aged Pd/Al_2O_3, fresh Pt/Al_2O_3 and aged Pt/Al_2O_3, respectively. At these temperatures, H_2S was added to the feed and the activity recorded as a function of time until the conversion did no longer vary with time. Then, the sulphur-free mixture was admitted to the catalysts and the activity recorded for several additional hours. The results are reported in Fig. 4.

Both Pd/Al_2O_3 catalysts are rapidly poisoned (Fig. 4), which leads to an almost complete loss of

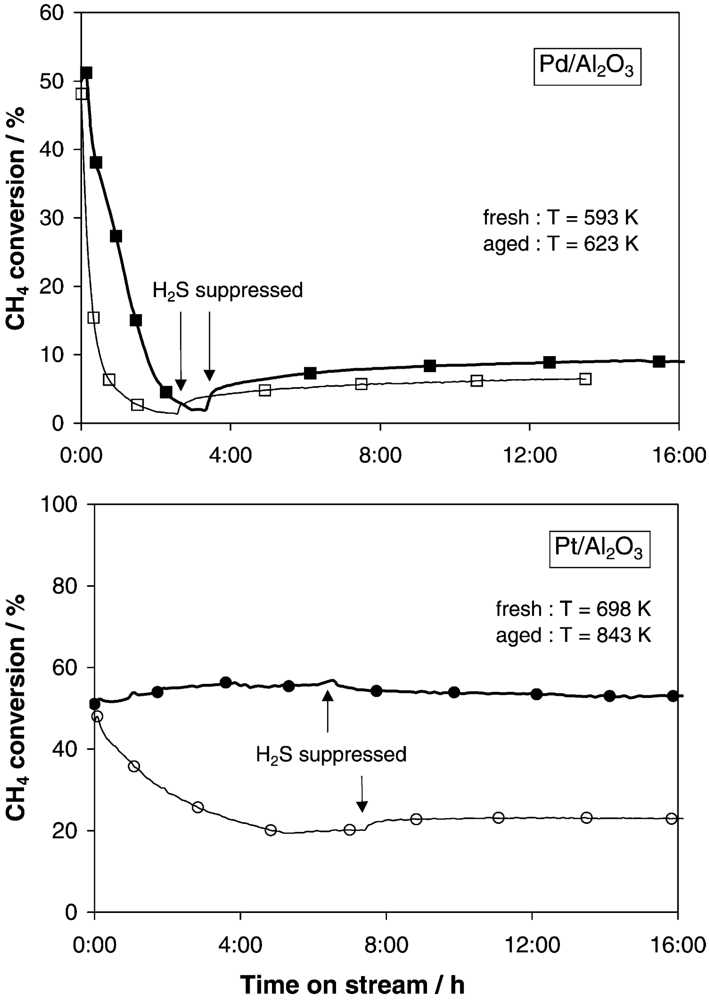

Fig. 4. Influence of 100 vol. ppm H_2S addition on methane conversion over fresh (open symbols) and aged (filled symbols) Pd/Al_2O_3 (□, ■) and Pt/Al_2O_3 (○, ●) catalysts vs. time on stream. Feed composition: 2000 vol. ppm CH_4; 5 vol.% O_2; He balance (200 mg catalyst; total flow rate of $6.5\,l\,h^{-1}$; GHSV = $20\,000\,h^{-1}$). The temperature of reaction was chosen so that approximately 50% conversion was reached in the sulphur-free dry feed.

activity in methane oxidation. A residual activity corresponding to less than 2% CH_4 conversion can be still detected for both catalysts. It can be also noticed that the poisoning is more rapid for the fresh catalyst than for the aged one. Upon switching to the sulphur-free mixture, the catalytic activity is only slightly and slowly restored. After 11 h exposure to the sulphur-free feed, the CH_4 conversion is, respectively, 6.5 and 9% for the fresh and aged catalysts. These results are consistent with a strong poisoning of Pd catalysts by sulphur containing compounds (H_2S or SO_2) observed in previous studies, irrespective of the support, being sulphating or non-sulphating [9,11,12,19,25–27]. It may be stated that, under lean conditions, H_2S is easily oxidised into SO_2/SO_3 species and that SO_3 species readily react with basic sites present at the surface of the catalyst, being either PdO surfaces sites or basic alumina surface sites, thus forming stable sulphate species. It is noteworthy mentioning that, in our experiments, H_2S was never detected, irrespective of the poisoning state of the catalyst. This indicates that the oxidation of H_2S into SO_x is easily achieved even on almost fully poisoned Pd catalysts. The transformation of active PdO sites into less active or inactive PdO–SO_x sites, observed in a study of sulphur poisoning of Pd/SiO_2 by IR spectroscopy [9], can be retained as the most likely explanation for the loss of catalytic activity in CH_4 oxidation of our Pd samples.

The influence of H_2S on the activity of Pt/Al_2O_3 catalysts in methane oxidation is much lower than for Pd catalysts. Introducing H_2S in the feed induces a slow moderate deactivation of the fresh Pt/Al_2O_3 catalyst until reaching a plateau at 20% CH_4 conversion, i.e. 42% activity loss with respect to the initial activity. The activity is then constant with time on stream and almost not changed when switching to the sulphur-free mixture. This corroborates the statement that Pt catalysts are more resistant to sulphur poisoning than Pd catalysts [19]. On the aged Pt catalyst, it is even surprising to observe a slight increase of the CH_4 conversion from 50 to 55% upon exposure to the sulphur containing mixture. The initial activity is then slowly recovered after suppressing H_2S in the feed. These results indicate that at this temperature, H_2S has no significant influence on the catalytic activity of Pt/Al_2O_3 in methane combustion.

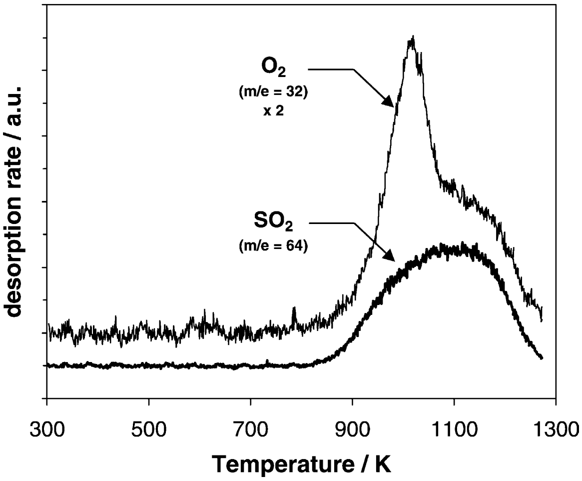

Fig. 5. TPD profiles of O_2 and SO_2 vs. temperature from fresh Pd/Al_2O_3 poisoned under H_2S containing reaction mixture at 593 K (600 vol. ppm O_2; He balance; flow rate of 20 cm^3 min^{-1}). Heating rate of 5 K min^{-1} (0.03 g of catalyst).

3.4. Stability of poisoning species on fresh Pd/Al_2O_3 and regeneration of activity in CH_4 combustion

The decomposition of poisoning species formed upon methane combustion in the presence of H_2S over fresh Pd/Al_2O_3 was studied by TPD experiment carried out in 600 vol. ppm O_2 in He. Fig. 5 shows the TPD profiles corresponding to SO_2 ($m/e = 64$) and O_2 ($m/e = 32$). SO_3 was never detected in the gas phase at the outlet of the reactor during the experiment. SO_2 evolved from the catalyst for temperatures between 873 and 1273 K, as revealed by a broad asymmetric peak with a maximum at ca. 1070 K. This indicates the progressive decomposition of sulphate species present at the surface of the catalyst and unstable at temperatures above ca. 870 K. Simultaneously to the formation of SO_2, the concentration in O_2 is observed to increase, indicating the release of O_2 from the catalyst. A sharp maximum is observed at ca. 1020 K and the O_2 desorption still continues at higher temperatures, resulting in a signal shape similar to that of SO_2. The sharp peak at ca. 1020 K is attributed to the decomposition of PdO into Pd. This interpretation was confirmed in a separate TPD experiment of the fresh non-poisoned PdO/Al_2O_3 catalyst in O_2/He, exhibiting the same sharp peak centred at 1020 K. It can be inferred from the O_2 signal shape that, in addition to the PdO decomposition, surface sulphate species decompose into SO_2 and O_2 evolved simultaneously from the catalyst, resulting in the broad signals, according to the equation:

$$\text{surface } SO_4{}^{2-} \rightarrow \text{surface } O^{2-} + SO_2 + \tfrac{1}{2}O_2 \qquad (1)$$

It is worthwhile noticing that the stoichiometry of the reaction (1) is fully consistent with the amount of desorbed O_2 deduced from our TPD experiments by subtracting the measured total amount of desorbed O_2 and the calculated amount of O_2 resulting from the complete PdO decomposition.

Different surface sulphate species might have formed during the catalytic test performed in the presence of H_2S, as proposed in previous studies [9,11,12,19]: one siting at the surface of the PdO particles and one siting at the surface of the alumina support. Hoyos et al. [9] studied the combustion of methane under oxidising conditions in the presence of H_2S. The formation of surface $PdSO_4$ species was observed by IR spectroscopy when Pd was supported on a non-sulphating support (SiO_2). The authors observed the decomposition of palladium sulphate species above 623 K in nitrogen, the decomposition being complete at 873 K [9]. Surprisingly, it appears from our experimental TPD data that SO_2 desorption starts above 873 K, i.e. at temperatures higher than that corresponding to the complete decomposition of palladium sulphate species indicated by Hoyos et al. [9]. This interesting point will be discussed further in the paper. At this stage, it can be concluded that TPD in O_2/He cannot allow to distinguish between possible different sulphate species present at the surface of Pd/Al_2O_3 after H_2S poisoning.

The regeneration of the catalytic activity of fresh-poisoned Pd/Al_2O_3 catalyst was then studied as follows. Two different fresh Pd/Al_2O_3 samples were poisoned by exposure to the reaction mixture containing H_2S at 593 K for 2 h and 30 min, exposed to the H_2S-free reaction mixture for 1 h, then flowed in 5 vol.% O_2/He, treated at 773 and 923 K, respectively, for 3 h, finally quenched at 593 K and exposed again to the H_2S-free reaction mixture for several hours at 593 K in order to measure the catalytic activity with time on stream and evaluate the regeneration percentage of the catalytic activity in CH_4 combustion. The results reported in Fig. 6 depict the regeneration percentage of the activity in CH_4 oxidation measured at 593 K as a function of time on stream after regeneration of the poisoned Pd/Al_2O_3 at 773 and 923 K in O_2/He.

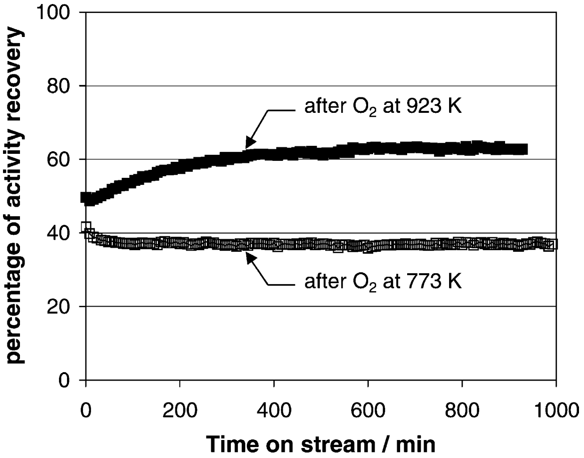

Fig. 6. Percentage of activity recovery measured at 593 K after a treatment of fresh H_2S-poisoned Pd/Al_2O_3 catalysts in 5 vol.% O_2/He at 773 K (☐) and 923 K (■) for 3 h. Feed composition: 2000 vol. ppm CH_4; 5 vol.% O_2; He balance (200 mg catalyst). Total flow rate of 6.5 l h^{-1}.

Upon regeneration at 773 K, the catalytic activity at 593 K varied slightly and very rapidly from a value corresponding to 42% of the initial activity (before poisoning) to 36% of the initial activity, and then remained constant with reaction time. This indicates that only a fraction of the active PdO surface sites was regenerated upon the treatment in O_2 at 773 K. Assuming the conversion is proportional to the number of active sites, which should be approximately fulfilled for conversions less than 50%, this would indicate that poisoning palladium sulphate species only partially decomposed, thus restoring 36% of the sites active for CH_4 oxidation. After reaction, the sulphur content estimated by IR spectroscopy was measured and found equal to 1.1 wt.% S. This value corresponds to that obtained after poisoning treatment, confirming that no sulphur was desorbed from the sample upon regeneration at 773 K in O_2/He as expected from TPD experiment. This indicates that sulphate species were partially re-distributed at the surface of the catalyst, migrating from PdO surface sites to alumina surface sites, without any loss of sulphur from the catalyst.

Upon regeneration at 923 K, the catalytic activity at 593 K varied very slowly from 55% of the initial activity up to 63% of the initial activity and then remained constant. It was checked that the regeneration treatment could not be responsible for any significant decrease of the catalytic activity by possible partial sintering of the PdO active phase. It should be pointed out that the catalytic activity measured during the very first minutes after contacting the regenerated sample with the reaction mixture is not much higher than that measured with the sample regenerated at 773 K. This would indicate that the treatment at 923 K was only slightly more efficient than the one at 773 K to release sulphate species from PdO surface and regenerate active sites. Once the catalyst was equilibrated in the reaction mixture after several hours, regeneration in O_2/He at 923 K induced much improved activity compared to the treatment at 773 K but has not yet allowed the complete regeneration of the catalytic activity. This could be surprising if considering that palladium sulphate species are highly unstable at 923 K, being expected to be fully decomposed upon the treatment. As expected from TPD experiment, the sulphur content measured by IR was equal to 1.0 wt.%, which represents a decrease of about 10% of the total amount of sulphate species contained in the non-regenerated catalyst. Thus, in spite of the decreasing amount of sulphate species at the surface of the catalyst and the expected complete decomposition of palladium sulphate species, it is clearly observed that only ca. 2/3 of the initial active sites were restored upon this severe O_2/He treatment, 1/3 being still poisoned by inactive sulphate species. These points will be developed in the following section.

A mechanism for the deactivation of PdO catalysts by sulphur oxides in lean-burn conditions was already proposed by Lampert et al. [19]. In this study, SO_2 was used instead of H_2S as sulphur containing compounds. SO_2 was proposed to convert on PdO into SO_3, SO_3 then adsorbing on PdO as sulphates. With a sulphating support like Al_2O_3, SO_3 was proposed to adsorb also on the support, thus protecting PdO and decreasing the rate of poisoning of the active PdO phase. Upon removal of SO_2 from the gas steam, the support was thought to spill back SO_3 onto PdO thus inhibiting the decontamination of the catalyst.

These ideas are mostly re-considered but additional new features must be taken into account in order to explain all our experimental data for the H_2S deactivation of PdO/Al_2O_3 catalysts and their regeneration in O_2/He. The suggested mechanism is illustrated in Fig. 7. We propose that the oxidation of H_2S into SO_2 is a “facile” reaction, so that H_2S is totally converted to SO_2, irrespective of the extent of catalyst deactivation with respect to CH_4 oxidation. As proposed by Lampert et al. [19], we suggest that, at low reaction temperatures (typically 600 K), SO_2 converts to SO_3 on PdO and that SO_3 adsorbs primarily on PdO, forming $PdSO_4$ species. These species are thought to migrate to the alumina support by a surface diffusion mechanism, therefore, being trapped on the strongly basic surface alumina sites in the neighbourhood of PdO particles. This process would decrease the rate of PdO poisoning as observed in previous studies. This also involves that, once the basic alumina sites located around the PdO particles are covered by sulphate species, the process of sulphate migration from PdO to Al_2O_3 would stop and the deactivation of PdO with respect to SO_2 and CH_4 oxidation reactions would be complete. The process would depend on Pd dispersion. It is expected that the sulphur content upon complete deactivation would be much less than at saturation of alumina by sulphates, and would not vary significantly with time on stream in H_2S containing feed, once the catalyst is deactivated. This hypothesis was confirmed by a long-term poisoning experiment in H_2S containing feed at 593 K. After 30 h of reaction in presence of H_2S, the sulphur content determined by IR was found equal to only 1.8 wt.% S, i.e. not drastically different from the S content measured after 2.5 h-poisoning (1.1 wt.% S).

Upon regeneration in O_2/He at 773 K, SO_3 desorbs from PdO surface as SO_2 and O_2 since $PdSO_4$ is thought to be partly decomposed at this temperature. On the other hand, SO_2 evolved from PdO surface would be re-oxidised into SO_3 on basic alumina sites [15,28,29], being more distant from PdO particles and still free from sulphate species. In other words, O_2 treatment at 773 K would induce the migration of SO_3 from PdO to the alumina by a gas phase diffusion process, thus leading to the re-distribution of sulphate species between PdO and alumina surface sites away from PdO particles. SO_2 cannot desorb from the catalyst, which agrees with the observed absence of loss of sulphur from the catalyst. Under reaction conditions, no significant further change is observed in sulphate distribution.

Upon regeneration in O_2/He at 923 K, SO_2 desorbs partially from the sample. Sulphate species linked to

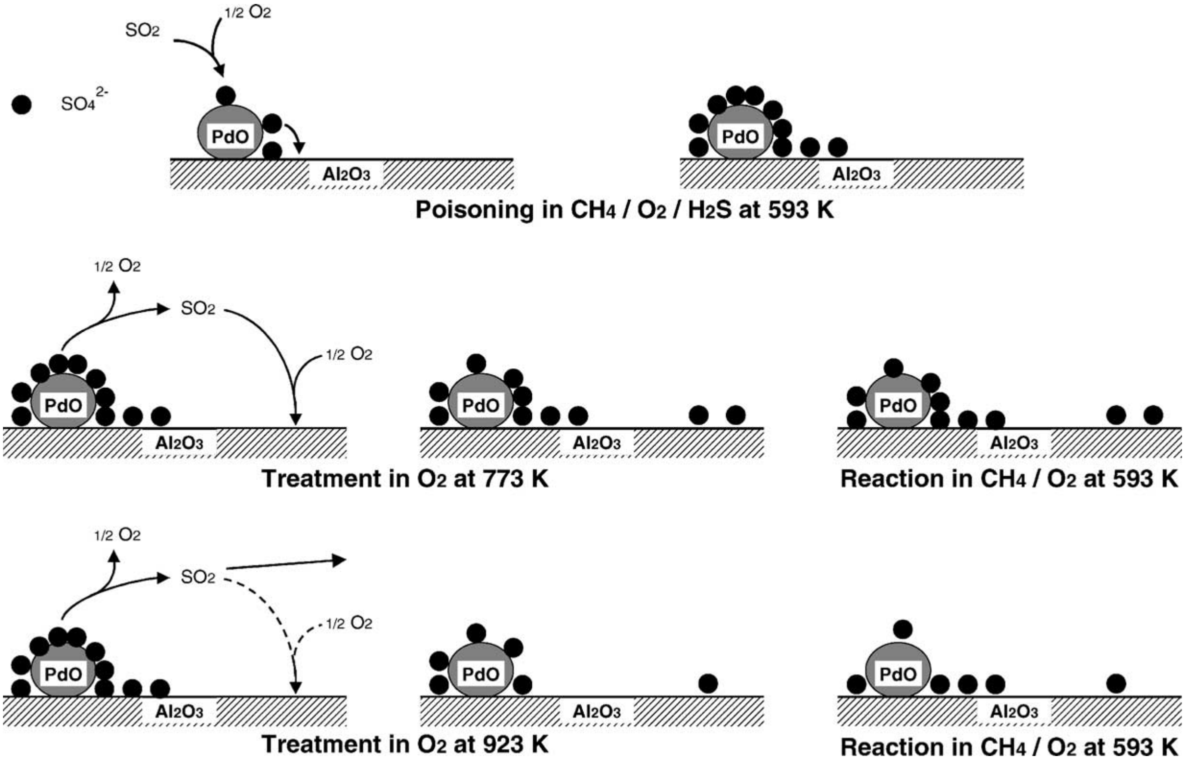

Fig. 7. Scheme of H_2S poisoning and regeneration mechanisms for Pd/Al_2O_3 catalysts. H_2S easily converts to SO_2. PdO oxidises SO_2 to SO_3. SO_3 is trapped by PdO and spills to Al_2O_3 sites surrounding the PdO particles by surface diffusion. At saturation of these sites, SO_3 poisons PdO by palladium sulphate formation. Under O_2 at 773 K, $PdSO_4$ slowly decomposes to PdO and $SO_2/(1/2)O_2$. SO_3 around PdO spills back to PdO. SO_2 can re-oxidise to SO_3 on basic alumina sites away from PdO particles and cannot evolve from the catalyst. SO_3 is re-distributed on the catalyst surface by gas diffusion. Under O_2 at 923 K, sulphate at alumina sites slowly decomposes into SO_2. SO_2 is slowly removed from the catalyst. The decomposition is catalysed by PdO and the concentration in SO_3 on Al_2O_3 around PdO decreases. On quenching, PdO surface is still partially covered by SO_3. Under reaction, SO_3 spills to Al_2O_3 sites around PdO. The activity increases until saturation of alumina sites by surface diffusion. The activity is not fully restored.

basic alumina surface sites are thought to slowly decompose at this temperature, the reaction being catalysed by PdO. The amount of sulphate species on the alumina in the neighbourhood of PdO particles decreases. But on quenching the catalyst at low temperature, the PdO surface would be still partially covered by sulphates. On exposure to the sulphur-free feed at 593 K, sulphate species trapped on quenching are supposed to slowly spill to alumina surface sites surrounding the PdO particles and available for trapping by surface diffusion because of partial desulphation. This would explain the progressive regeneration during further reaction in the sulphur-free feed until reaching again the saturation of alumina sites surrounding PdO particles by sulphate species, thus suppressing the surface diffusion process from PdO to Al_2O_3.

4. Conclusions

Without water or H_2S added to the feed, Pd/Al_2O_3 catalysts exhibit, compared to Pt/Al_2O_3, the best catalytic activity in the oxidation of methane traces under lean-burn conditions. The superiority of Pd over Pt is even larger when comparing catalysts aged in the presence of water at 873 K, i.e. in moderate ageing conditions, chosen to simulate long-term ageing for lean-burn NGV application. This is partly due to the better resistance of Pd against sintering. The presence of 10 vol.% water vapour in the feed causes a strong decrease of the catalytic activity of the fresh and aged Pd catalysts and the fresh Pt catalyst. The activity is restored by suppressing the water supply. This behaviour is attributed to a competition between water and methane for the active sites. In wet stream, the superiority of Pd over Pt is reduced due to a stronger inhibition of water on the catalytic activity of Pd in methane oxidation compared to Pt. Exposure to H_2S induces a strong and irreversible deactivation of Pd catalysts, while Pt catalysts are more resistant. For the fresh H_2S-poisoned Pd/Al_2O_3 catalyst, the presence of sulphate species is revealed. These species are presumably located both on PdO and on the basic alumina sites in the neighbourhood of PdO particles. A poisoning mechanism of Pd/Al_2O_3 by progressive formation of inactive $PdSO_4$ species is thus suggested. Although palladium sulphate species are known to fully decompose below 873 K, sulphate species present on the H_2S-poisoned Pd/Al_2O_3 catalyst are shown to decompose in O_2/He only above 873 K. It is deduced that below 873 K and above ca. 673 K, sulphate species are re-distributed at the surface of the catalyst. Accordingly, active PdO sites are partly regenerated and the extent of the catalytic activity recovery increases with the increase of temperature of the treatment in O_2/He. However, although sulphate species are partly removed from the catalyst, a treatment in O_2 at temperatures as high as 923 K does not allow the complete regeneration of the catalytic activity of the H_2S-poisoned Pd/Al_2O_3. It is suggested that, while being not completely removed from the catalyst, sulphate species can migrate back and forth between PdO and basic alumina sites, depending on the temperature, therefore preventing the complete regeneration of the catalyst with respect to methane oxidation.

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