

Barium Promoted Palladium Catalysts for the Emission Control of Natural Gas Driven Vehicles and Biofuel Combustion Systems

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Pd/ and Pd–Ba/alumina catalysts were prepared and tested for their activities in the removal of pollutants released from stoichiometrically operated natural gas vehicles (NGVs) and from the combustion of biofuels in small-scale stoves. The addition of barium to the Pd/alumina catalyst resulted in improved fresh and aged activities by widening the lambda window in NGV applications and by lowering the $T_{50\%}$ for methane in biofuel combustion applications. An attempt to slow down the detrimental effect of sulfur toward methane oxidation was carried out by arranging Pd–Ba/alumina, Ba/alumina, and Pd/alumina in three separate layers. Ba species were believed to act as a sulfur sink or trap, leaving the active PdO partially free for methane oxidation. XPS technique was used to investigate the nature of sulfur species on the catalyst as well as the state of the precious metal. In addition, the catalysts were characterized by means of XRD, XRF, H₂-adsorption, N₂-physisorption, SO₂/O₂/C₁₀H₈-TPD, and CH₄-TPR. © 2002 Elsevier Science (USA)

Key Words: catalytic oxidation; palladium; barium; catalyst aging; sulfur poisoning; NGVs; biofuels.

INTRODUCTION

The use of alternative energy sources such as natural/biogas and wood residuals is becoming increasingly attractive both for economic and environmental (decreased CO₂ generation) consideration. The stable methane molecule is a main constituent in the emissions released from both natural gas driven vehicles (NGVs) and the combustion of wood (biofuels). This enables a joint development of catalysts suitable for these types of applications. It is widely accepted that palladium catalysts offer the highest activity in the removal of methane emitted from various sources. Sulfur poisoning and thermal decomposition of palladium species, however, limit the use of Pd only supported on, e.g., alumina. Ambitious emission targets such as ULEV, ELEV,

and EURO4 affect both the design and the position (close coupled systems) of the catalytic converter, which in turn puts new requirements on the hydrothermal stability of the materials as the precatalyst is placed close to the manifold of the engine (1).

Barium oxide is usually added to alumina-supported palladium catalysts in order to improve the catalysts' performance under severe hydrothermal conditions (2, 3). The promotion effect of BaO has been explained by its capacity to retain large surface areas of alumina effectively, because the added cations occupy the surface sites or bulk sites to prevent atomic diffusion (surface diffusion and bulk diffusion), which brings about the α phase transformation (4). In a bimetallic Pd–Ba three-way catalyst the Ba component was reported to result in improved hydrocarbon oxidation under reducing conditions, because the alkaline earth metal suppressed the hydrocarbon chemisorption on the Pd catalysts and therefore allowed the catalytic reaction to proceed smoothly (5).

Engström *et al.* (6), discussed the interaction between sulfur dioxide and NO_x storage catalysts in a recent paper. They found that the SO₂, from the gas feed was accumulated as sulfates in the catalyst, which was considered to depend on the high affinity of barium species for sulfation. In another work (7), it was proven that palladium on sulfating supports (e.g., γ -alumina) deactivates more slowly and can tolerate more sulfur since the SO_x is also adsorbed onto the carrier.

In this work we show the promotional effect of barium on Pd/alumina in terms of gaining improved hydrothermal stability, higher resistance to the sulfur poisoning effect, and a wider lambda window. In addition, we present a proposal for a catalytic concept in biofuel combustion applications, where the catalyst has been arranged in three layers in order to trap and slow down the detrimental effect of sulfur toward active PdO species. A detailed XPS study has been carried out, dealing with the state of the noble metal, possible interactions between Pd and Ba, and the type of sulfur related species on the surface.

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EXPERIMENTAL

Preparation of Catalysts

A commercial γ -alumina (LaRoche, Versal GL-25) was used as the catalyst support. The received alumina was precalcined at 900°C for 8 h as a preventive measure against the severe hydrothermal conditions taking place during the activity screening. This procedure led to a surface area drop from 247 to 149 m²/g. In addition to the γ -phase, the presence of a δ -phase and to a lesser extent an α -phase of alumina, were detected by XRD technique over the precalcined support. Low (1 wt%) and high (3 wt%) palladium loaded Pd–Ba/alumina catalysts were prepared by introducing 15 wt% of barium (C₄H₆BaO₄, Fluka, >99%) on the precalcined alumina via the incipient wetness method. The obtained Ba/alumina material was dried for 12 h in air (90°C) and calcined at 550°C for 3 h. Palladium addition to the Ba/alumina was carried out by adsorption from a solution of preacidified PdCl₂ (Johnson Matthey, 99.8%). The filtered Pd–Ba catalysts were dried for 12 h at 90°C and finally the materials were calcined at 550°C for 3 h. A reference 3 wt% Pd/alumina catalyst was prepared using the techniques described above. The prepared catalysts were named with their respective metal loadings given in parentheses prior to the formulation as: (1.0,15.0)Pd–Ba/alumina, (3.0,15.0)Pd–Ba/alumina, and (3.0)Pd/alumina.

Activity Screening of Catalysts

a. Catalytic aftertreatment of emissions released in small-scale biofuel combustion. The flow system for testing the catalysts for the removal of simulated pollutants released from small-scale biofuel combustion consisted of pressure regulators, mass flow controllers, valves, filters, a preheater for nitrogen, a naphthalene saturator, and a water evaporator. The naphthalene, which was chosen as a model poly-aromatic hydrocarbon (PAH), was brought to the system by passing CO₂ through a naphthalene bed, which was kept at 42.5°C. Water was added into the system using a IVACP 6000 Medical Systems syringe pump combined with a heated evaporator, which was further driven by oxygen. The nitrogen was preheated prior to mixing with the other gases. The catalyst granules (250–500 μ m) were packed in a vertical Inconnel tube reactor placed in a Carbolite furnace, which in turn was connected to a Eurotherm temperature controller. Analyses of the gases leaving the reactor (or the catalyst) as well as the by-passed (calibration) gases, were performed in an online Hewlett Packard 9500 gas chromatograph equipped with a 30 m DB1 column, a FID, and a 6-way heated sampling valve and a HC–CO–CO₂ NDIR gas analyzer. All the lines after the preheater, evaporator, and naphthalene saturator as well as the lines from the reactor to the GC were heated. The temperatures were

TABLE 1

The Composition of the Gas Mixtures

Component	Gas mixture 1 ^a (Biofuel)	Gas mixture 2 ^b (NGV)
CH ₄	200 ppm	400 ppm
NO	—	500 ppm
C ₁₀ H ₈	50 ppm	—
CO	2500 ppm	7000 ppm
CO ₂	12 vol%	10 vol%
O ₂	10 vol%	varied ^c
H ₂ O	12 vol%	6 vol%
H ₂	—	800 ppm
N ₂ /He	Balance	Balance

^a For biofuel emissions, total flow = 2100 ml/min, GHSV = 20000 h⁻¹.

^b For NGV application, total flow = 400 ml/min, GHSV = 50000 h⁻¹.

^c Varied for different lambda values.

measured by thermocouples axially placed in the reactor immediately before and after the catalyst bed.

The catalysts were tested in four consecutive light-off cycles in the temperature window of 120–800°C and with a heating rate of 3°C/min (GHSV = 20000 h⁻¹ and total volume flow = 2100 ml/min) using the gas mixture 1 in Table 1. The testing procedure was carried out as follows: (1) Light-off testing of the fresh catalyst (cycle 1). (2) Consecutive aging of the catalyst under the flow of reactants at 800°C for 6 h. (3) Cooling of the catalyst to room temperature in excess air. (4) Repeated light-off testing of the catalyst (cycle 2). (5) Hydrothermal aging of the catalyst at 850°C for 16 h in 12 vol% steam. (6) Cooling of the catalyst to room temperature in air. (7) Third light-off test of the catalyst (cycle 3) and consecutive cooling of the substrate in air. (8) Final light-off test in the presence of 5 ppm SO₂ in the gas feed mixture (cycle 4).

In a separate test, the catalyst granules were arranged in three layers in order to investigate the possibility of trapping the detrimental sulfur components in one or two layers. This arrangement consisted of a (1.0,15.0)Pd–Ba/alumina catalyst followed by a (15.0)Ba/alumina layer. In the final layer a 1 wt% Pd only catalyst was used. The believed mechanism in this catalyst concept is that sulfur dioxide entering the first catalyst would get oxidized to SO₃ and SO₄ species, which additionally would form stable barium sulfate in the first and second layer. If most of the sulfur were attached in the first layers, the last catalyst would perhaps be partially unaffected considering the active PdO species (especially regarding the sensitive methane combustion). The layered catalyst was subjected to the four cycles defined above. In addition, this concept was also tested in a fifth consecutive cycle, in the presence of 5 ppm of sulfur in the gas feed, where the temperature was kept constant at 500°C and the concentration changes of methane were analyzed. In this test sulfur was added into the feed for 8 h with an intermediate “regeneration” (sulfur shut-off) of 1 h after

3 h. It must be noted that the total amount of palladium in the layered catalyst was half of that of the (3.0)Pd and (3.0,15.0)Pd–Ba catalysts.

b. Catalytic removal of pollutants emitted from NGVs. In this part of the study, the catalyst activities in the conversion of a gas mixture simulating the emissions from NGVs (gas mixture 2, Table 1) were examined. The catalyst granules, 250–500 μm , were tested in a temperature interval of 120–600°C and with a heating rate of 2°C/min (GHSV = 50000 h⁻¹). Both fresh and aged (subjected to the four cycles defined earlier for biofuel applications) catalysts were tested in slightly rich ($\lambda = 0.99$) and lean ($\lambda = 1.01$) conditions. In addition, the Pd and Pd–Ba/alumina catalysts were checked for their activities in stationary lambda sweep tests at 450°C. This test included a stepwise change of lambda values (lean–rich–lean) in a lambda range of 0.98–1.03. Some of the aged (4 cycles) catalysts were cooled down in the rich gas mixture for XPS characterization purposes in order to investigate possible PdS formation under reducing conditions. A test rig consisting of a quartz-micro reactor placed in a furnace equipped with a temperature controller was applied in the screening of the materials. The temperature in the catalyst bed was monitored by a K-type thermocouple connected to a Eurotherm 900 EPC. All the gases were introduced into the reactor by means of mass flow controllers. The water was added to the gas mixture by a liquid flow (Bronkhorst HI-TEC) controller, which was combined with a controlled evaporator mixer (Bronkhorst HI-TEC). Gases were preheated before entering the reactor and the temperature in the pipes was kept constant with heating resistances. Oxygen was led separately into the reactor in order to avoid a reaction between NO and O₂ before entering the catalyst bed. CO and CH₄ conversions were determined using an HP 6890 gas chromatograph equipped with a FID, a TCD, a Porapak Q column, and a molecular sieve 5A column. The concentrations of NO_x (NO + NO₂) were measured by means of chemiluminescence analysis (PPM Systems). The gases used in both types of applications (a and b) were of the highest purity commercially available.

Catalyst Characterization

XRD patterns of the alumina support were recorded on a Philips PW1830 diffractometer equipped with a PC-IDENTIFY software databank. The metal content analyses of the catalysts, which had been dissolved in a mixture of HF and Aqua Regia in a high performance microwave oven (Milestone mls 1200 mega) under elevated pressure conditions, were carried out using XRF technique (X-MET 880, Outokumpu Electronics).

A Perkin–Elmer 5400 ESCA and an Omicron surface science system (located at the University of Turku, Finland) with Mg K α source and 35 eV pass energy were used in the XPS analysis of fresh, aged and sulfur poisoned samples. The binding energy (BE) calibration was based on C 1s

peak at 284.6 eV. The accuracy of the analyzed binding energies was ca. ± 15 eV. Impurities other than carbon were not observed. Approximately 5 eV of charging was detected during the X-ray bombardment of the samples. No changes in the charging was observed during measurement and the pressure was typically 1×10^{-8} Torr. In order to increase the confidence in the computer fit, both peaks of spin-orbit spectral envelopes were included in the peak fitting procedure. The intensity ratios and energy separations were kept fixed at their theoretical values. The Voigt function, which is a convolution of Gaussian and Lorentzian lines, was used in the peak fitting. Prior to the Voigt function fitting, the background caused by inelastically scattered photoelectrons, was removed using Shirley's method (8). The sensitivity factors used in quantitative analysis for Al 2p, Ba 3d_{5/2}, La 3d, O 1s, and Pd 3d were 0.234, 7.469, 9.122, 0.711, and 5.356 for PHI 5400 ESCA, and 0.2046, 6.73, 8.109, 0.711, and 4.844 for the Omicron system; respectively.

Adsorption Studies

The metal dispersions and mean particle sizes of palladium on alumina and Ba/alumina were determined by hydrogen adsorption at 90°C (Carlo Erba Instruments 1900) at the pressure range of 1–100 Torr. During the back adsorption method, the amount of the reversibly adsorbed gases on the catalysts was measured. The Langmuir method was used for calculating the palladium dispersion and mean particle size on the fresh and sulfur poisoned catalysts. N₂-physisorption experiments were performed with a Carlo Erba Instrument 1900 in order to measure the BET surface areas of the received and precalcined alumina support.

The O₂/C₁₀H₈/SO₂ temperature programmed desorption (TPD) studies were carried out in a volumetric flow apparatus including a quartz micro reactor inserted in a temperature controlled furnace. Prior to the O₂-TPD experiments, the fresh and aged Pd and Pd–Ba samples were “cleaned” at 200°C for 30 min and cooled to room temperature in a mixture of argon and nitrogen. The catalyst temperature was then linearly increased to 800°C (5°C/min) with a 30 min dwell at the final temperature.

In the naphthalene-TPD experiments, the samples were pretreated in N₂/Ar flow at 200°C for 30 min. After cooling to 25°C the catalysts were subjected to 380 ppm of C₁₀H₈ for 1 h, flushed (1 h) and the TPD experiment was performed in the 25–600°C temperature range with a heating rate of 5°C/min.

The SO₂-TPD was carried out as follows: (1) Pretreatment of alumina, Ba/alumina, Pd/alumina, and Pd–Ba/alumina in 1013 ppm of SO₂ in N₂ in the 25–400°C temperature range (10°C/min) including a 2 h dwell at the final temperature. (2) Cooling of the catalysts in 1013 ppm SO₂ in N₂ to room temperature. (3) Flushing of the catalyst surfaces for 30 min. (4) TPD measurements of the materials in the 25–800°C range (10°C/min). All evolved gases, in the TPD

experiments mentioned above, were analyzed by means of quadrupole mass spectrometry (Carlo Erba Instruments).

Temperature Programmed Reduction

The CH₄-TPR experiment was carried out in the test rig presented under the subtitle named “Catalytic removal of pollutants emitted from NGVs.” In addition to the experimental setup described, a Carlo Erba Instruments 1900 quadrupole mass spectrometer was connected to the outlet of the quartz reactor in order to measure the evolved gases from the catalyst surface. Prior to the TPR experiment, the catalyst was treated in air at 400°C for 30 min. After cooling in air with consecutive flushing in helium flow (30 min), the TPR was performed in the presence of 1 vol% CH₄ in the 25–600°C temperature range.

RESULTS AND DISCUSSION

a. Catalytic aftertreatment of emissions released in small-scale biofuel combustion. The results from the activity testing of the alumina supported Pd and Pd–Ba catalysts, in the removal of pollutants (methane, carbon monoxide, and naphthalene) released from a simulated 35 kW small-scale wood stove, are given in Figs. 1 and 2 as well as in Table 2. As can be seen the fresh catalysts (in cycle 1) exhibited high efficiencies in the aftertreatment of the unwanted components and complete removal of all the three reactants was already obtained at approximately 470°C. In the presence of steam, in the two aging procedures (i.e., under the reactants

flow at 800°C for 6 h and under hydrothermal conditions at 850°C for 16 h), the 3 wt% reference Pd/alumina catalyst underwent a slight deactivation in terms of increased T_{50%} in methane from 381°C over the fresh catalyst to 431°C over the hydrothermally treated catalyst. Almost no deactivation toward CO oxidation was observed over the same catalyst. In naphthalene conversion, however, some lost activities were seen in cycles 2 and 3. The naphthalene oxidation activity over the (3.0)Pd/alumina differed slightly from the corresponding Pd–Ba formulation, as there was a drastical “wave” like behavior in the conversion curve (Fig. 1) at temperatures below 170°C. Over the (3.0, 15.0)Pd–Ba catalyst this drop and the increase in the naphthalene conversion was not recorded and the activity was high already at the first experimental point. This phenomenon is discussed in more detail in the adsorption studies section.

The (3.0,15.0)Pd–Ba/alumina formulation showed high hydrothermal stability in the oxidation of all three reactants. Especially pronounced was the stability for total oxidation of methane, where only small changes in the T_{50%} values were recorded in the three first cycles (Table 2 and Fig. 2). During the second cycle even some activation in the methane oxidation activity was observed and the T_{50%} dropped from 359°C in the first cycle to 333°C. The conversion of CO and naphthalene to CO₂ over the (3.0,15.0)Pd–Ba/alumina formulation exceeded 70%, in the two first cycles, already at the starting temperature. In the third cycle, however, some deactivation of CO and C₁₀H₈ oxidation was detected.

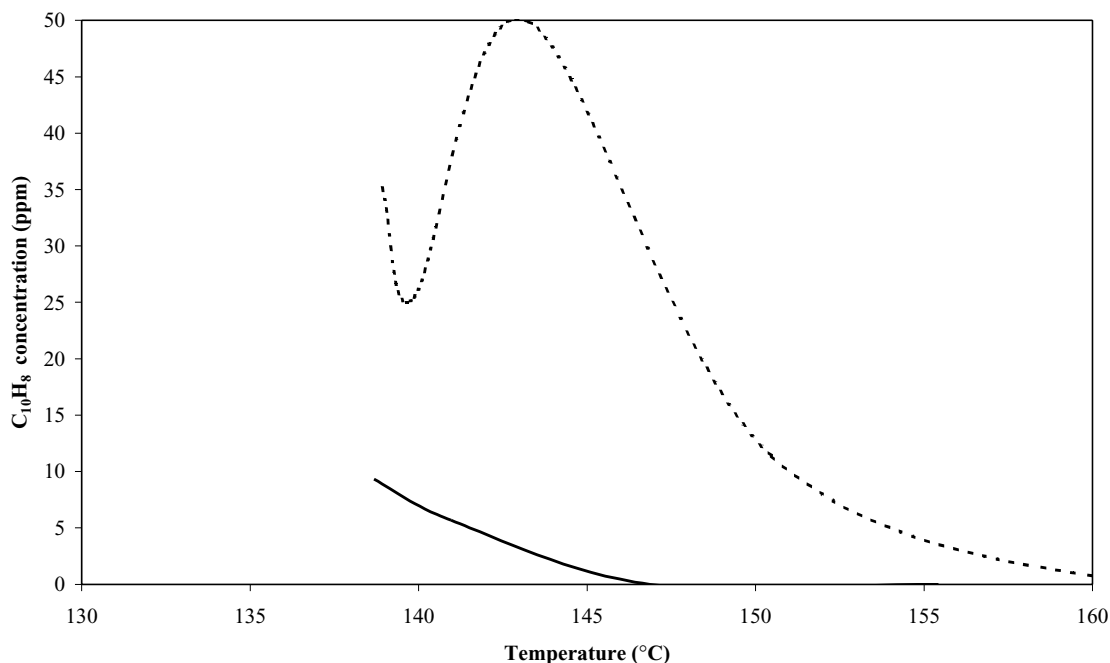


FIG. 1. Naphthalene concentration profile in test cycle 1 over (3.0,15.0)Pd–Ba/alumina (solid line) and (3.0)Pd/alumina (dashed line). Gas mixture 1 in Table 1 and Pd mass = 0.105 g.

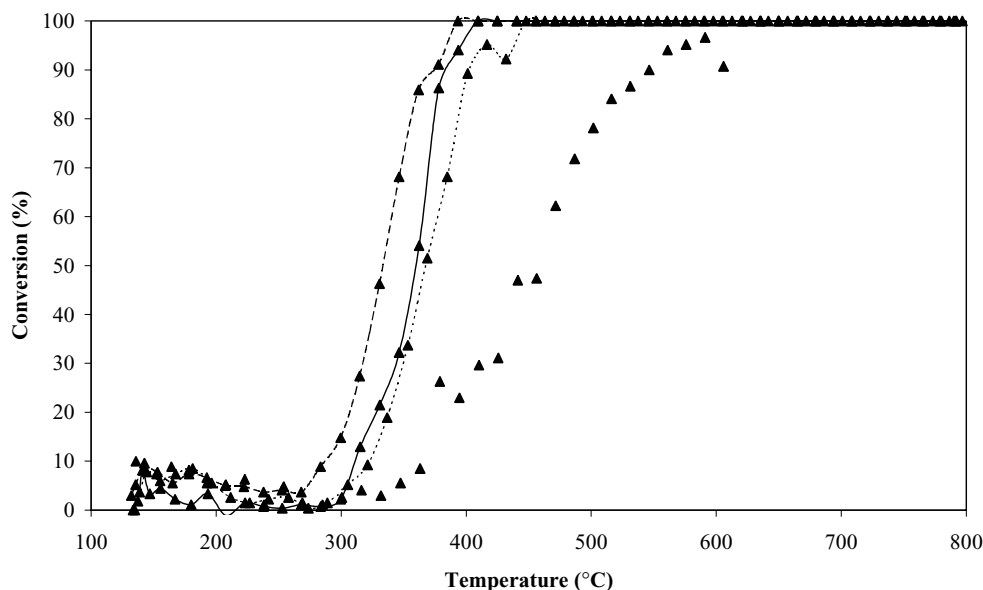


FIG. 2. Conversion of CH_4 to CO_2 over (3.0,15.0)Pd–Ba/alumina in biofuel combustion applications. Solid line, cycle 1; broken line, cycle 2; dashed line, cycle 3; no line, cycle 4. Gas mixture 1 in Table 1 and Pd mass = 0.105 g.

The low palladium loaded (1.0,15.0)Pd–Ba/alumina also exhibited high activities in converting the pollutants to CO_2 and H_2O , both in fresh and aged forms. The fresh activity of this catalyst was similar to that of (3.0)Pd/alumina in terms of methane oxidation. Surprisingly, comparable with the two first cycles, activation in the conversion of methane into carbon dioxide was detected in the third cycle. A somewhat more pronounced deactivation toward CO was seen

TABLE 2

$T_{50\%}$ Light-Off Results over Catalysts Tested in the 4 Cycles Defined for Biofuel Applications in (a)

Catalyst	Cycle	CH_4 (°C)	CO (°C)	C_{10}H_8 (°C)
(3.0,15.0)Pd–Ba/alumina; Pd mass = 0.105 g	1	359	<139	<139
	2	333	<132	<132
	3	368	149	<134
	4	459	167	135, 164
(3.0)Pd/alumina; Pd mass = 0.105 g	1	381	<139	148
	2	407	142	164
	3	431	143	139, 163
	4	511	149	not measured
(1.0,15.0)Pd–Ba/alumina; Pd mass = 0.035 g	1	398	<137	<137
	2	417	<139	153, 172
	3	390	166	148
	4	547	173	132
“3 layered application”: Pd–Ba/ \Rightarrow Ba/ \Rightarrow Pd/alumina; Pd mass = 0.0525 g	1	400	<138	<138
	2	386	136	<135
	3	404	150	144
	4	437	157	137

Note. Metal content is given in parenthesis prior to catalyst. Gas mixture 1 in Table 1.

(cycle 3) over this low loaded binary catalyst compared with the (3.0)Pd/alumina caused by the hydrothermal conditions.

The addition of sulfur into the feed gas mixture resulted in a drop of activities in methane oxidation over all three catalysts (Table 2). When comparing the fresh and sulfur-poisoned catalysts, the increase in the $T_{50\%}$ of methane was typically over 100°C in every test run. The highest activity of methane oxidation in the presence of sulfur (for the “ordinary” arranged catalysts) was recorded over the (3.0,15.0)Pd–Ba/alumina substrate, with a $T_{50\%}$ of 459°C. This temperature was approximately 50 and 90°C lower than observed over the corresponding (3.0)Pd/alumina and (1.0,15.0)Pd–Ba/alumina; respectively. The sulfur effect on the activity toward CO and C_{10}H_8 oxidation was less pronounced and full conversions of these reactants were obtained below 200°C over all the three poisoned catalysts.

In a separate test using the 3 layered-catalyst, high oxidation activities of CH_4 , CO, and C_{10}H_8 were obtained both in fresh and in aged form (Table 2). The removal of methane in the presence of sulfur was extremely good ($T_{50\%} = 437^\circ\text{C}$) and the increase in the light-off temperature from fresh to sulfur poisoned catalyst was only 37°C. In the fifth cycle, the long-term effect of sulfur on the 3 layered-catalyst concept was investigated at 500°C (Fig. 3). Here, a slow deactivation toward methane oxidation was recorded after approximately 0.5 h. The initial conversion reaching 90% dropped down to ca. 40% where it stabilized. After being subjected to sulfur for 3 h the catalyst was “regenerated” in the base gas mixture 1 in Table 1 for 1 h. The methane conversion rose immediately to high levels (above 90%)

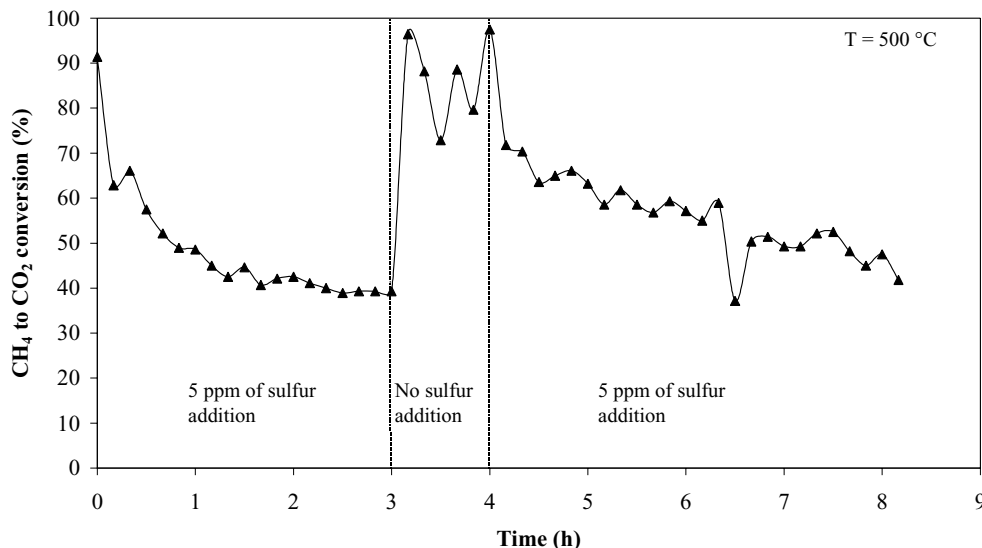


FIG. 3. Methane to CO₂ conversion over the 3 layered (Pd-Ba/alumina ⇒ Ba/alumina ⇒ Pd/alumina) catalyst in the presence and absence of 5 ppm of SO₂. Gas mixture 1 in Table 1 and Pd mass = 0.0525 g.

with some intermediate fluctuations. The readdition of sulfur again resulted in lowered activities in methane oxidation and slowly the conversion fell down to ca 40% level after a 4 h dwell. It should be stressed that the Pd content of this 3 layered concept was half that of the (3.0Pd/alumina and (3.0,15.0)Pd-Ba/alumina.

b. Catalytic removal of pollutants emitted from NGVs. The results from the catalyst testing for NGV applications are given in Tables 3 and 4 and in Figs. 4 and 5. In the light-off tests, using the fresh Pd and Pd-Ba catalysts, high oxidation activities of CH₄ and CO were obtained both under lean $\lambda = 1.01$ and rich $\lambda = 0.99$ conditions. The temperature for T_{50%} of methane, as opposed to the biofuel applications, was lower (328°C) over the fresh Pd/alumina than the Pd-Ba/alumina (352°C) under lean conditions. At temperatures above 350°C a drop in the CO conversion under rich conditions was observed, which was significantly more pronounced over the Pd only catalyst than the Pd-Ba/alumina. In our previous work (9), we showed that the

oxidation of carbon monoxide and methane is thermodynamically restricted. However, the drop in CO conversion over the Pd only catalyst exceeds by far the thermodynamic restrictions. This could probably depend on the water-gas shift or steam reforming reaction starting to compete with the desired total oxidation of CO.

In the rich light-off runs over the aged (subjected to 4 cycles in biofuel applications) Pd/alumina catalyst, lost activities in methane oxidation were recorded at temperatures exceeding 450°C. At this temperature the conversion of methane dropped sharply and at the end temperature (600°C), the catalyst did not convert more than 20% of CH₄ into CO₂. Conversely, over the aged Pd-Ba catalyst, no decline in methane oxidation was detected. As mentioned in the Introduction, the addition of Ba to a Pd supported catalyst promotes the hydrocarbon oxidation activity, especially during reducing conditions (5).

The conversion of NO, over both fresh and aged catalysts, was low during the lean light-off tests, not reaching conversion levels higher than approximately 30%. On the rich

TABLE 3

Lean ($\lambda = 1.01$) T_{50%} Light-Off Results over Pd and Pd-Ba/Alumina for NGV Applications Using the Gas Mixture 2 in Table 1

Catalyst	CH ₄ (°C)	CO (°C)	NO (°C)
(3.0)Pd/alumina (fresh)	328	176	Not reached
(3.0,15.0)Pd-Ba/alumina (fresh)	352	172	Not reached
(3.0)Pd/alumina (aged ^a)	381	179	Not reached
(3.0,15.0)Pd-Ba/alumina (aged ^a)	381	178	Not reached

^a Catalyst has been subjected to 4 cycles defined for biofuel applications in (a).

TABLE 4

Rich ($\lambda = 0.99$) T_{50%} Light-Off Results over Pd and Pd-Ba/Alumina for NGV Applications Using the Gas Mixture 2 in Table 1

Catalyst	CH ₄ (°C)	CO (°C)	NO (°C)
(3.0)Pd/alumina (fresh)	418	215	172
(3.0,15.0)Pd-Ba/alumina (fresh)	411	203	201
(3.0)Pd/alumina (aged ^a)	430	215	215
(3.0,15.0)Pd-Ba/alumina (aged ^a)	405	196	231

^a Catalyst has been subjected to 4 cycles defined for biofuel applications in (a).

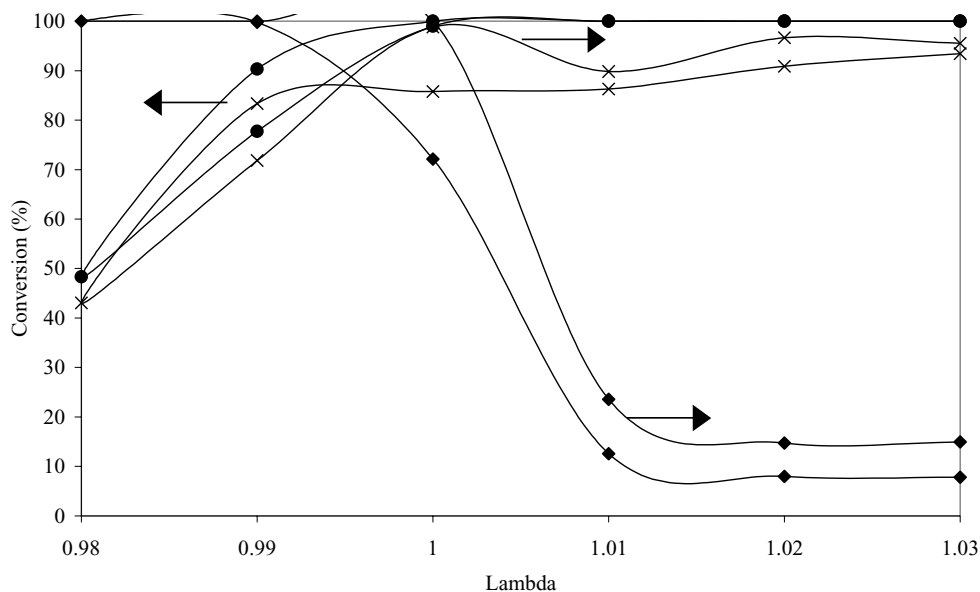


FIG. 4. Stationary lambda sweep experiment over aged* (3.0,15.0)Pd-Ba/alumina at $T = 450^{\circ}\text{C}$ using the gas mixture 2 in Table 1. (x) CH_4 ; (●) CO ; (◆) NO ; (*) subjected to 4 cycles defined for biofuel combustion applications in (a). Arrow indicates direction of sweep.

side, as expected, complete removal of NO was achieved at temperatures above 270°C . The maximum in NO removal coincided with high oxidation rates of CO , indicating the $\text{NO} + \text{CO}$ interaction and/or $\text{NO} + \text{H}_2$ reaction.

In the stationary lambda sweep tests at 450°C , the highest activities in the removal of the three reactants (CO , CH_4 , and NO) were obtained at $\lambda = 1$ and $\lambda = 0.995$ over the aged (4 cycles) Pd/alumina and Pd-Ba/alumina; respectively (Figs. 4 and 5). A hysteresis effect in the conversion of CH_4 and NO was observed over both catalysts. This be-

havior may depend on the restructuring/phase changes of palladium species on the surface when sweeping from lean-rich-lean. A somewhat wider lambda window was recorded over the binary Pd-Ba catalyst than over the Pd only catalyst. Here again, the promotion effect of barium seems to be important under substoichiometric conditions.

Within the framework of the following subtitles a correlation between characterization, adsorption, and reduction studies and the catalyst performances will be presented and discussed.

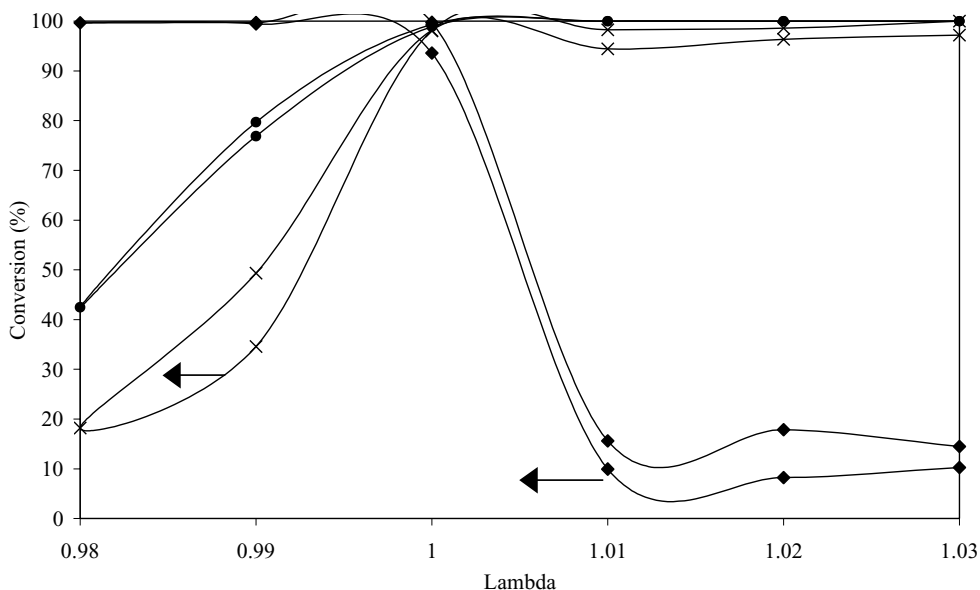


FIG. 5. Stationary lambda sweep experiment over 4 cycles aged* (3.0)Pd/alumina at $T = 450^{\circ}\text{C}$ using the gas mixture 2 in Table 1. (x) CH_4 ; (●) CO ; (◆) NO ; (*) subjected to 4 cycles defined for biofuel combustion applications in (a). Arrow indicates direction of sweep.

TABLE 5

Pd Dispersion and Pd Mean Particle Size Measured by H₂-Adsorption at 90°C

Catalyst	Pd dispersion (%)	Mean particle size of Pd (Å)
(3.0)Pd/alumina fresh	56.1	20.1
(3.0)Pd/alumina aged ^a	30.2	37.3
(3.0,15.0)Pd–Ba/alumina fresh	82.1	13.7
(3.0,15.0)Pd–Ba/alumina aged ^a	59.0	19.1

^a Subjected to 4 cycles defined for biofuel combustion applications (a).

Characterization

The dispersions and mean particle sizes of palladium on the fresh and aged (subjected to the 4 cycles defined in the biofuel combustion applications) are presented in Table 5. As can be seen, the Pd dispersion (82.1%) on the fresh (3.0,15.0)Pd–Ba/alumina was significantly higher than on the reference Pd only catalyst (56.1%). The mean particle size of palladium on the fresh (3.0,15.0)Pd–Ba/alumina was also smaller (13.7 Å) than on the reference formulation (20.1 Å). To investigate the possibility of irreversible hydrogen adsorption on Ba, which in turn might affect the Pd dispersion measurements, we performed an additional H₂-chemisorption experiment over the fresh Ba/alumina. In this experiment we observed that, although small amounts of hydrogen adsorbed on Ba/alumina, the majority was reversibly adsorbed and the amount of irreversibly adsorbed hydrogen was much less (1.03 Ncm³/g metal) than the corresponding Pd–Ba/alumina (86.57 Ncm³/g metal). This small amount could only affect the Pd dispersion maximum by unity. The hydrothermal treatment combined with the sulfur poisoning during the 4 cycles resulted in lost Pd dispersions and in growth of the mean particle sizes of Pd. Again

both higher dispersion (59.1%) as well as smaller particles of Pd (19.1 Å) were calculated on the (3.0,15.0)Pd–Ba catalyst than on reference catalyst (30.2%, 37.3 Å). The growth in the Pd particle size can also be seen in the Pd/Al XPS ratios (Table 6). It is widely accepted that the addition of ceria to supported precious metal catalysts gives rise to improved dispersion. Here it appears that the same effect can be obtained with Ba and in addition a high hydrothermal resistance is gained. In the transactions (10) of Yantai University, an improvement, by ceria and barium, on the dispersion, isolation, and stabilization of Pd active components on alumina, was reported. In their work on the effect of additives on the surface area of oxide supports for catalytic combustion, Machida *et al.* (11) found that BaO mixed with Al₂O₃ (forming barium hexaaluminate) exhibited outstanding effect in maintaining a large surface area up to 1600°C, especially when the proper preparation method was applied (hydrolysis of alkoxides). In another work by Johnson (12), it was concluded that increasing the concentrations of phosphorus, silicon, barium, strontium, or tin on an alumina catalyst increased the area stabilization in terms of a decreased rate of area loss. In our BET surface area measurements we saw a slight stabilization effect by barium over the Ba/alumina sample compared to the un-promoted alumina (13 vs 19 m²/g). The surface areas of fresh alumina (149 m²/g) and fresh Ba/alumina (102 m²/g) dropped over the corresponding steamed samples (850°C, 16 h) to 130 m²/g and (89 m²/g); respectively. The promotional effect of Ba, in terms of surface area stabilization should be more pronounced at temperatures higher than 1000°C as shown in Ref. (11) and (12). The promotional effect of barium on the hydrothermal stability of alumina seems to be one of the reasons for obtaining higher dispersion and smaller particle size of Pd on the fresh and aged (3.0,15.0)Pd–Ba/alumina as compared to the reference Pd only catalyst. Compared with the reference material the

TABLE 6

XPS Analyzes over Fresh, Aged, and Sulfur Poisoned (3.0)Pd/Alumina and (3.0,15.0)Pd–Ba/Alumina

Catalyst	Pd 3d _{5/2} BE (eV)	Ba 3d _{5/2} BE (eV)	Al 2p BE (eV)	S 2p _{3/2} BE (eV)	Pd: Al (at.%)	Ba: Al (at.%)	S: Al (at.%)
F: (3.0)Pd/alumina	336.2		73.8		0.0052		
A: (3.0)Pd/alumina	336.6		74.0	168.9	0.0017		0.0015
F: (3.0,15.0)Pd–Ba/alumina	334.2 ^a	780.3	73.8		0.017	0.046	
	336.0 ^b						
H: (3.0,15.0)Pd–Ba/alumina	336.2	780.3	73.6		0.012	0.11	
A: (3.0,15.0)Pd–Ba/alumina	334.3	780.4	73.9	168.8	0.0037	0.060	0.011
S: (3.0) Pd/alumina	334.6		74.1	168.7	0.0044		0.033
S: (3.0,15.0) Pd–Ba/alumina	334.5	780.5	74.0	168.6	0.014	0.028	0.059
N: (3.0)Pd/alumina	334.9		74.1	168.7	0.0011		0.039
N: (3.0,15.0)Pd–Ba/alumina	334.8	781.0	74.4	169.0	0.0031	0.040	0.011

Note. F: fresh catalyst; A: subjected to 4 cycles in application (a); H: subjected to 3 cycles in application (a); S: subjected to 1013 ppm of SO₂ in the temperature range of 25–400°C (2 h dwell at 400°C); N: subjected both to 4 cycles in application (a) as well as light-off tests + lambda sweep in application (b), where final test run was performed under reducing conditions at λ = 0.99.

^a 45%.

^b 55%.

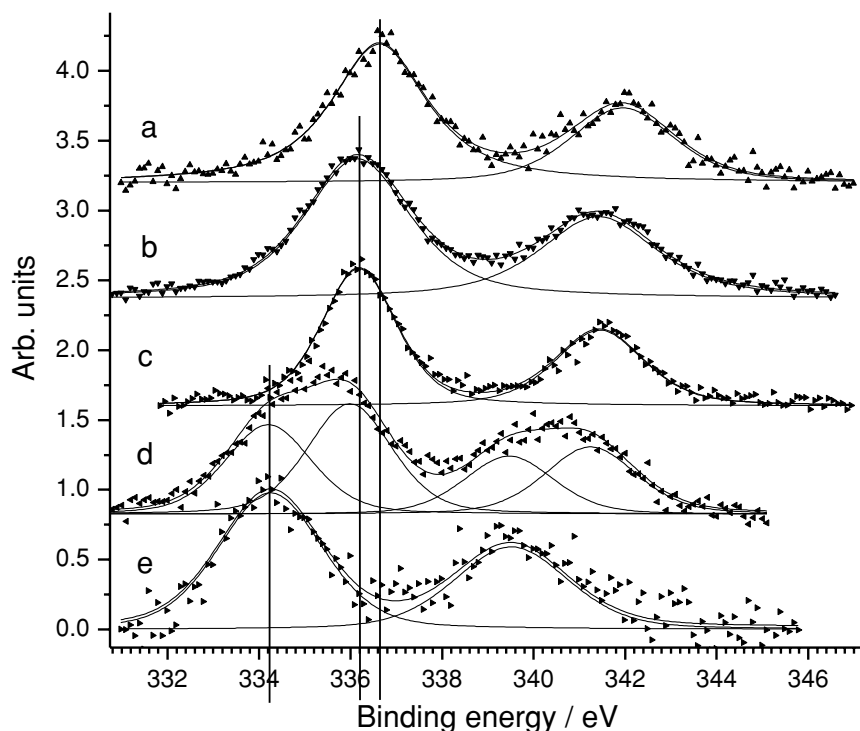


FIG. 6. Pd 3d XPS lines of Pd and Pd-Ba/alumina catalysts. (a) aged* (3.0)Pd/alumina; (b) fresh (3.0)Pd/alumina; (c) aged** (3.0,15.0)Pd-Ba/alumina; (d) fresh (3.0,15.0)Pd-Ba/alumina; (e) aged* (3.0,15.0)Pd-Ba/alumina; (*) catalyst has been subjected to 4 cycles in application (a); (**) catalyst has been subjected to 3 cycles (hydrothermal treatment) in application (a).

higher activity of the binary Pd-Ba catalyst, in the total oxidation of methane, can be correlated to the improved dispersion and smaller particles of palladium.

The results from the XPS analyses are given in Table 6 and Fig. 6. Palladium binding energy (BE) values slightly above 336 eV are typical to +2 oxidation state in PdO (13–15). Palladium in the fresh (3.0,15.0)Pd-Ba/alumina catalyst existed in two states, with 336.0 and 334.2 eV BEs. The peak at 336.0 eV is at a slightly lower BE than the corresponding peak (336.2 eV) of the fresh (3.0)Pd/alumina catalyst, due to the alkaline earth metal interaction, which is in agreement with previous studies on this topic (5). We attribute the peak at 334.2 eV to a stronger charge transfer from the BaO, which is a base oxide (electron pair donor), to the small (13.7 Å) PdO species on the surface, resulting in negatively charged PdO, which may show as metallic Pd in XPS analysis. In their study on the promotional effect of Ba on Pd/alumina catalysts, Kobayashi *et al.* (16) detected that the BE value of Pd 3d_{5/2} measured over their Pd-Ba/alumina catalyst was shifted to a lower value (between PdO and metallic Pd). They explained this phenomenon by an electron density increase around PdO in Pd-Ba/alumina. Owing to the hydrothermal conditions, as the Pd particle size grows, the charge transfer becomes of less importance and is limited to the PdO/Ba interface and therefore the BE returns back to the values corresponding to bulk PdO

(BE = 336 eV). The electronic properties of small particles are strongly affected by the environment. In fact, Joyner *et al.* (17) by theoretical calculations showed that electronic perturbations at the interface between metal and support extend only a short range of no more than 0.5 nm into the particle. In the freshly calcined catalyst the mean metallic Pd diameter was found to be ca. 1.3 nm. This means that, based on Joyner's calculations, a considerable fraction of the PdO particles on the Pd-Ba/alumina catalyst can readily be affected by the presence of an electron donor (BaO). This electron donation results in decreased BE value of Pd 3d_{5/2}. The aged Pd-Ba catalyst was slightly sintered owing to hydrothermal conditions (mean diameter = 1.9 nm). In this case the XPS data clearly indicated the presence of only PdO species. Although the sintering of palladium is little, it appears to be enough to minimize the effect of electron transfer (or it might be that only the surface of the PdO particle is negatively charged, and the bulk is exhibiting oxide BE characteristics). Xiao *et al.* (18), reported a two shoulder phenomenon on the XPS pattern of a Pd/alumina catalyst, where the feature at 335.5 eV was attributed to an electron deficient Pd particle located at an acidic site on Al₂O₃ and the other at 334.8 eV was shown to be far from the acidic site. In the Pd and Pd-Ba/alumina catalysts studied at our laboratory, this effect was barely visible.

According to Waqif *et al.* (19), surface SO₃ on pure Al₂O₃ is rather easily decomposed. Therefore, the sulfur related peak is most likely due to PdSO₄ (168.8 eV, (20)), BaSO₄ (168.9 eV, (21)) and/or Al₂(SO₂)₃ species, supported by the S 2*p*_{3/2} BE value slightly below 169 eV. The presence of so-called sulfones should also be mentioned as their binding energy values are close to those of sulfates. The total oxidation of hydrocarbons during the four light-off cycles is, however, very effective and therefore formation of hydrocarbon radicals (from naphthalene), which are attached to the sulfur species is rather unlikely.

The samples exposed to SO₂ (i.e., samples A, N, and S) exhibited BEs of palladium different than those attributed to palladium oxide. Sulfur 2*p*_{3/2} BE values detected at 168.6–169.0 eV are in agreement with the PdSO₄ XPS results reported by Matsumoto *et al.* (20). They also reported a palladium 3*d*_{5/2} PdSO₄ line at 337.3 eV, which was not observed in the present study. The reason might be that the PdO signal from beneath of the surface PdSO₄ skin overlaps the weaker surface palladium sulfate signal. The interaction of SO₂ with the catalysts is believed to take place via abstraction of oxygen from the PdO resulting in SO₃ generation leaving reduced Pd sites (Pd⁰). This reduced metallic palladium can further act as an oxygen dissociation site, which provides additional formation of SO₃. SO₃ is a reactive component and can energetically react with basic oxides to form the corresponding sulfate as in this case BaSO₄ and Al₂(SO₄)₃. Sulfur trioxide can as well react with the neighboring PdO species resulting in the formation of rather stable PdSO₄. We believe that on the Ba promoted catalyst, the SO₃ formed over palladium spills over to the barium oxide component and to a lesser extent on the alumina substrate. It appears that BaO acts as a sink for SO₃. Therefore, beside PdO and PdSO₄, a considerable metallic palladium is expected to be present on the Pd–Ba/alumina formulation. On the Pd/alumina sample SO₃ depletion is less and hence formation of PdSO₄ is considered to be more probable. Indeed, the XPS data (Table 6) indicated a line at 334.3 eV corresponding to metallic palladium over the Pd–Ba/alumina catalyst (sample A), whereas the line at 336.6 eV, which is believed to represent a PdSO₄ skin on the top of PdO (compared to 336 eV for PdO), was observed on the Pd/alumina catalyst (sample A). The fresh catalysts, which were subjected to 1000 ppm SO₂ at 400°C (in the absence of an oxidizer), exhibited the domain presence of metallic palladium (BE = 334.5 eV). The existence of metallic palladium on the N samples was expected and is a consequence of the final testing of these catalysts, which was performed under reducing conditions ($\lambda = 0.99$).

The BEs at 780.3–780.5 eV, of the fresh and aged Pd–Ba formulations (samples F, H, A, and S), indicates either BaO or BaSO₄. The shift to higher BEs here seems to represent the effect of sulfur reacting with the Ba component.

A higher shift (780.5 eV) was observed when the catalyst was subjected to ca. 1000 ppm SO₂.

The Pd/Al ratios were found to decrease by different hydrothermal treatments, which is in good agreement with decreased Pd dispersions (increased particle sizes). The Pd/alumina sample had a lower atomic ratio than the binary Pd–Ba catalyst, which also is believed to be the consequence of its lower dispersion. The amount of surface Pd lost during the 4 light-off cycles in the biofuel combustion application, was actually slightly higher for the barium promoted sample (A: (3.0,15.0)Pd–Ba/alumina) than for the Pd only sample (A: (3.0)Pd/alumina), which is in accordance with previous work (22). This seems slightly to contradict the H₂-chemisorption results. However, the thick Ba layer in between Pd and alumina probably affects these results.

A comparison of the S/Al ratios of the samples A reveals that there is a tenfold amount of sulfated species (formed during cycle 4) on the surface of the Pd–Ba/alumina catalyst compared with the Pd/alumina. In the Pd/alumina sample the formed sulfates are probably migrated to subsurface layer, being less detectable in XPS analysis. When these samples were reduced (samples N) a surface enrichment of S-compounds was detected on the Pd/alumina catalyst. There was no change in the S/Al ratio of the binary catalyst during the same reducing treatment. The reason lies most probably in the stability of the formed barium sulfate species. The mobility of S-species appears to be higher in the Pd/alumina sample compared with Pd–Ba/alumina, which is in accordance with observations by Xiao *et al.* (18), where they demonstrated a self-regeneration property of sulfur poisoned Pd/alumina catalyst, when subjected to the presence of H₂–O₂. The sulfate species are strongly anchored to barium (Pd–Ba/alumina), and in such concept resulting in less mobile S-species. The samples that were treated with 1000 ppm SO₂ (samples S) have a high S/Al ratio, which most probably lies in the fact that the samples are near sulfur saturation.

Adsorption Studies

In order to investigate the effect of the addition of Ba on the decomposition of highly active PdO species at elevated temperatures, O₂-TPD experiments were carried out over (3.0)Pd/alumina and (3.0,15.0)Pd–Ba/alumina. The results of this study are presented in Figs. 7 and 8. Quite different types of oxygen evolution patterns were detected over the fresh catalysts. The O₂-TPD over the fresh Pd–Ba catalyst resulted in only one broad peak with a maximum at approximately 735°C. In the O₂-TPD over the fresh Pd/alumina, twin peak behavior was recorded with maximum at 690 and 790°C. When studying the oxygen evolution patterns of the aged (4 cycles) Pd–Ba/alumina and Pd/alumina, we observed a significant decrease in the decomposition temperatures of PdO, as the temperatures for maximum peak

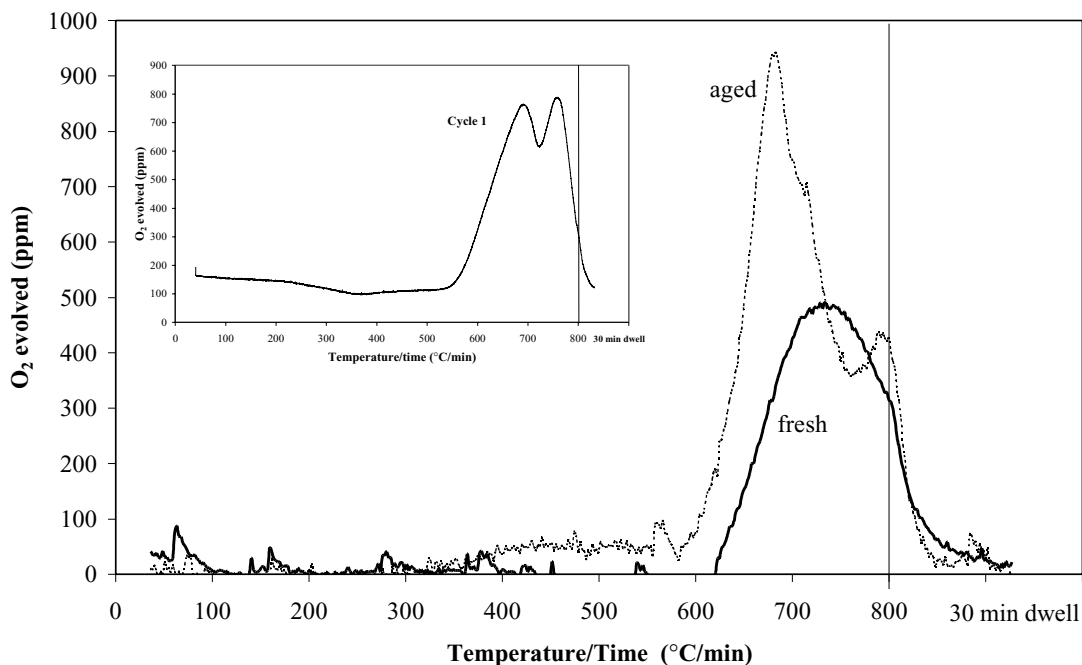


FIG. 7. O_2 -TPD experiment over aged (subjected to 4 cycles) and fresh (3.0,15.0)Pd-Ba/alumina. Upper left corner: O_2 -TPD pattern of (3.0, 15.0)Pd-Ba/alumina subjected to first cycle.

outputs were decreased by some 50 and 100°C; respectively. A second peak at higher temperatures (close to 800°C) was seen in the O_2 -TPD experiment over (3.0,15.0)Pd-Ba/alumina. The drastic change of the O_2 -TPD patterns between fresh and aged materials could be a result of the

rather complicated thermal chemistry of palladium, which was dealt with in a study by Farrauto *et al.* (23). They concluded that a reoxidation of Pd takes place after being exposed to high temperatures when a Pd/alumina catalyst is cooled down below 650°C, causing redispersion of PdO on

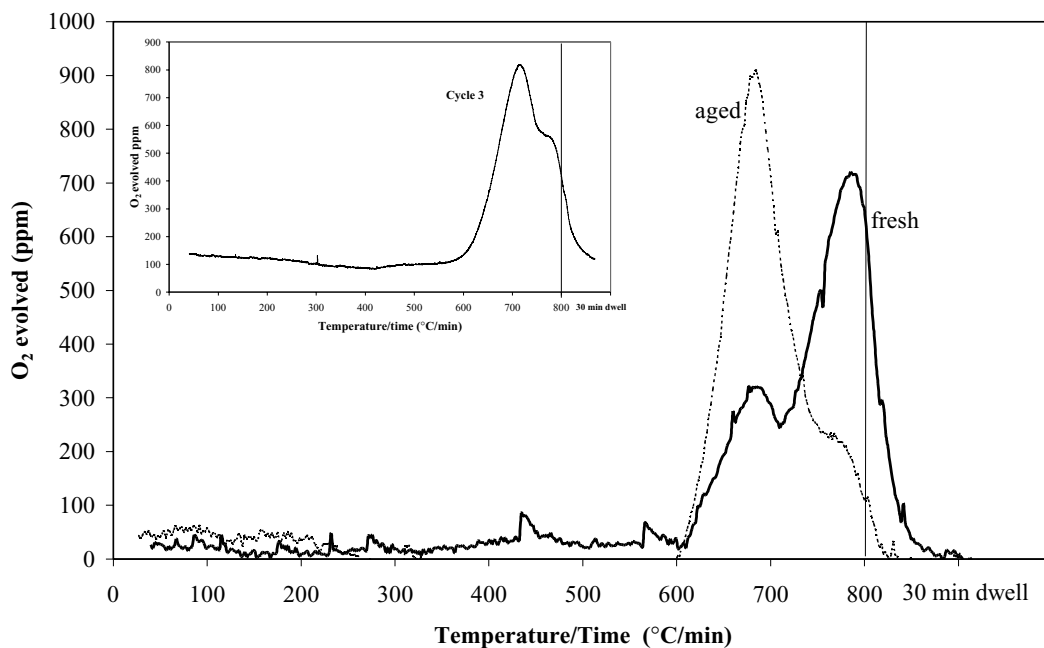


FIG. 8. O_2 -TPD experiment over aged (subjected to 4 cycles) and fresh (3.0)Pd/alumina. Upper left corner: O_2 -TPD pattern of (3.0)Pd/alumina subjected to 3 cycles.

alumina as well as the formation of PdO_x-Pd/alumina. The decomposition temperatures were shown to change for the redispersed PdO species. In another work by Lyubovsky *et al.* (24), the authors found that decomposition of PdO leads to the formation of large Pd metal particles. Upon cooling, these Pd particles reoxidize by the formation of rough poly-crystalline PdO particles, rather than by the formation of uniform layers of Pd oxide on the Pd metal. They concluded from these observations that the catalyst must undergo slow restructuring under reaction conditions to expose low-index surfaces that are apparently more reactive for methane oxidation. The changes in our O₂-TPD patterns from fresh to aged materials most probably depend on the restructuring of the surface. The same kind of twin-peak pattern, as in cycle 4, was observed already after the first cycle over the Pd-Ba formulation, however, the peak proportions were different. After the first cycle the low and high temperature peaks were almost equal in size. Further aging (cycles 2 and 3) resulted in increased fraction of the low temperature peak at the expense of the higher temperature peak. In our recent study (9) dealing with Pd-Ce/alumina catalysts, we discussed the possible existence of a crystalline and amorphous type of palladium oxide on alumina promoted by the addition of ceria. In that study, we observed strong twin peak behavior over both fresh and aged Pd-Ce/alumina, which we attributed to relate to crystalline and amorphous Pd. Ceria was believed to promote the formation of crystalline PdO, which has been reported to be more easily reduced (25). Here, the same behavior is observed over the fresh Pd/alumina and the aged Pd and

Pd-Ba/alumina, which is also believed to depend on the formation of different PdO phases.

In the second and third test cycles over the Pd-Ba/alumina catalysts (1 and 3 wt% Pd) an activation of the methane conversion was recorded. This activation could be a result of the formation of a highly redispersed rough Pd surface (discussed above) promoted by the presence of barium during the ageing procedure under reactants flow and hydrothermal conditions. The cause for activation may also be in the removal of chlorine species (originated from the metal precursor) from the surface, when exposed to steam. This is very unlikely, since such activation should have been also observed over the Pd/alumina catalyst. As was discussed in (25), the formation of crystalline and amorphous PdO during reaction conditions may result in a highly active catalyst for methane combustion. It appears that this kind of transformation is promoted by the presence of Ba, as the broad O₂ evolution peak from the fresh Pd-Ba catalyst is turned into two separate peaks over the aged catalyst.

The results of the naphthalene-TPD experiments over (3.0)Pd/alumina and (3.0,15.0)Pd-Ba/alumina are presented in Fig. 9. The strongest CO₂ formation was recorded at approximately 280°C over both of the catalysts, the binary Pd-Ba catalyst resulting in a stronger signal. Also a second CO₂ evolution peak at higher temperatures was observed at 460°C (Pd-Ba catalyst) and 500°C (Pd catalyst). The maximum in naphthalene evolution (280°C) over the Pd-Ba material coincided with the maximum CO₂ formation, indicating desorption and consequent combustion of naphthalene via oxygen abstraction from the PdO. Over

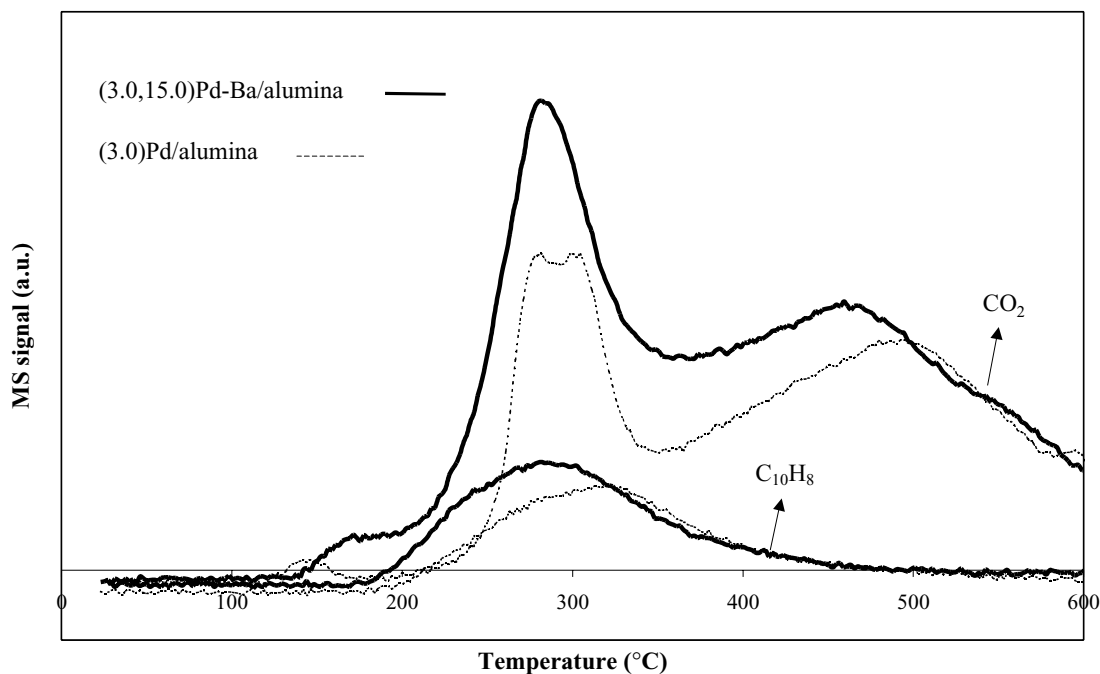


FIG. 9. C₁₀H₈-TPD experiment over fresh (3.0)Pd/alumina dashed line and (3.0,15.0)Pd-Ba/alumina (solid line).

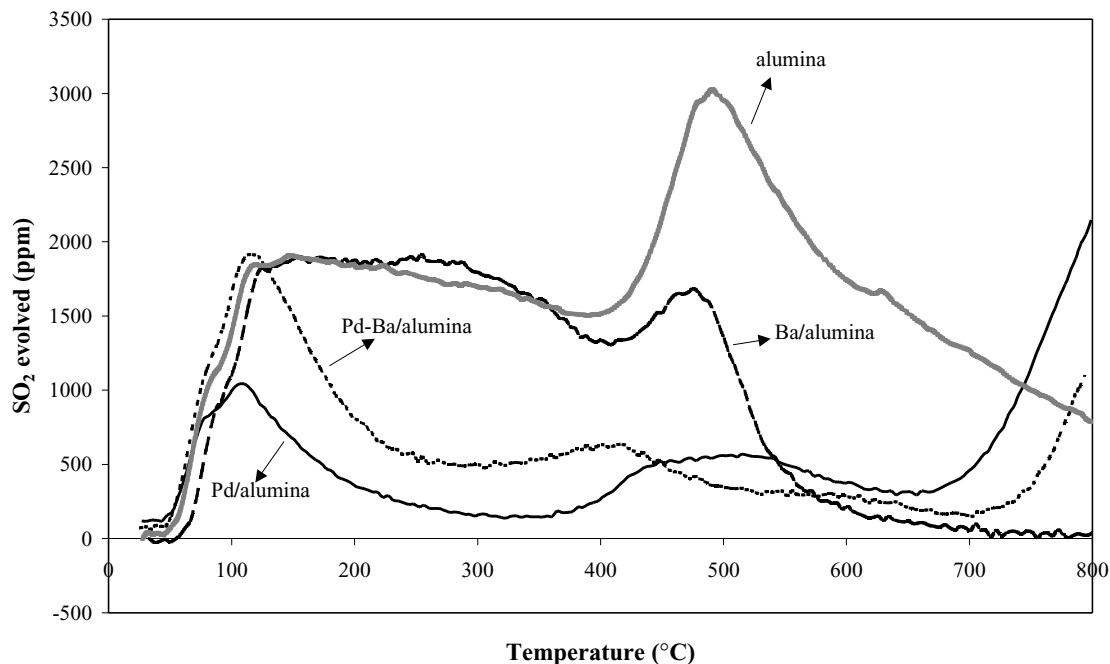


FIG. 10. SO_2 -TPD experiments over alumina, (15.0)Ba/alumina, (3.0)Pd/alumina, and (3.0,15.0)Pd-Ba/alumina.

the Pd only catalyst, however, the maximum in naphthalene evolution was shifted to higher temperatures (320°C) compared with the corresponding CO_2 peak. Shinjoh *et al.* (5), as mentioned already in the Introduction, showed that the addition of alkaline (e.g., Ba, Mg, Ca, Sr) to the Pd catalyst increases the electron density of palladium on the catalyst and weakens the adsorption strength of hydrocarbons on Pd. Further, they concluded that the addition of the alkaline earth metal suppresses the hydrocarbon chemisorption on the Pd catalyst and therefore allows the catalytic reaction to proceed smoothly. These observations are in good agreement with the results obtained both in the light-off test cycles (1–4) as well as in the C_{10}H_8 -TPD experiments, where higher activity in C_{10}H_8 to CO_2 oxidation was detected over the Pd-Ba formulation compared with the Pd/alumina catalyst. Especially pronounced are the differences between the two catalysts in the first light-off test cycle (Fig. 1), where over Pd-Ba/alumina an almost complete removal of naphthalene is obtained at low temperatures. Naphthalene removal over the Pd/alumina catalyst, on the contrary, seems to go through a strong adsorption step, followed by slower desorption/oxidation steps.

The shift in the CO_2 formation pattern (in the C_{10}H_8 -TPD experiments), over the Pd-Ba catalyst compared with the Pd/alumina catalyst, suggests a weakened Pd-O bond strength caused by the addition of BaO. The low temperature CO_2 formation pattern over the Pd/alumina catalyst exhibited a twin peak behavior, which is another indication of the presence of two types of PdO species having

different reduction character. This is in agreement with the data obtained from the O_2 -TPD experiments over the fresh Pd/alumina catalyst.

The results from the SO_2 -TPD experiments over alumina, (15.0)Ba/alumina, (3.0)Pd/alumina, and (3.0,15.0)Pd-Ba/alumina are presented in Fig. 10. Remarkable differences in the patterns of evolved SO_2 from the surfaces of the investigated catalysts and supports were observed. Three SO_2 peaks at 120, 420 (broad), and 800°C (final temperature) were recorded over the Pd-Ba/alumina. Also in the case of the Pd only catalyst, three distinctive peaks were obtained at 110, 523 (broad), and 800°C (final temperature). Higher amounts of SO_2 were desorbed from the Pd-Ba catalyst at the low temperatures (50–200°C) compared with the Pd/alumina. In contrast, at the final temperature, the highest SO_2 release took place over the Pd/alumina catalyst. Quite different SO_2 patterns were received over the supports (alumina and Ba/alumina), where high amounts of SO_2 were released from the surface in the temperature window of 50–400°C. At elevated temperatures (480–490°C) a sharp SO_2 peak was detected over both the supports, the stronger peak appearing over alumina.

In the case of the two supports, the SO_2 evolved at the starting temperatures could be a result of deposited multilayer of SO_2 , which has been reported to desorb at low temperatures (26). As the catalyst temperature rises considerably, SO_2 release from formed aluminum sulfates is believed to take place. On Ba/alumina the existence of formed “ultra stable” barium sulfates might affect the SO_2 pattern, because some of the sulfur species have reacted

with the BaO forming sulfates and thereby lowering the amount of SO₂ desorbed in the TPD experiment. Decomposition of barium sulfate was reported to begin at 1000°C over a BaSnO₃ catalyst (27). In the same work, the authors concluded that once sulfates are formed, their fixation to BaSnO₃ is irreversible and thus poisoning is rendered inevitable. It has been reported (19), that on pure alumina, two types of surface sulfate species are formed. The first is more stable at a low surface coverage attributed to a type with 1 double S : O bond and the second less stable and more easily decomposed by water vapor, attributed to an SO₃ group linked to an Al–O pair site or to an oligomer species as S₂O₇. The authors also showed that, in the presence of oxygen, Cu on alumina performs the first step of oxidation of SO₂ to SO₃, which then forms a stable surface sulfate at either the Cu site or the Al site. This is in agreement with the differences in the peak positions stemming from the believed decomposition of aluminum sulfate on the supports and the catalysts. It seems that aluminum sulfates formed via palladium promotion are more stable than those formed on pure alumina and Ba/alumina. In another work, where palladium supported on Al₂O₃, MgO, and TiO₂ was treated with H₂S, H₂ + O₂ or O₂, Xiao *et al.* (18), concluded that the strong acidity of alumina affects its surface oxygen species in such a direction that the negatively charged sulfur ions are not adsorbed and transformed on Pd/alumina as easily as in the case of Pd supported MgO and TiO₂. They also implied that so called self-regeneration with H₂–O₂ is more likely to take place on the Pd/alumina than on the two other formulations discussed above. This self-regeneration ability of alumina might partly explain the higher amounts of sulfur released from the surface of alumina and Pd/alumina at higher temperatures compared with the Ba promoted formulations.

The SO₂ peaks at low temperatures (110–120°C) released from Pd and Pd–Ba/alumina are most probably due to loosely bound SO₂ on the Pd surface. As discussed previously the interaction of SO₂ with PdO (in the absence of oxygen) results in the generation of metallic Pd-species. The observed low temperature SO₂ desorption peaks are therefore SO₂ adsorbed on metallic palladium. The Pd–Ba/alumina catalyst, having a higher Pd dispersion and metallic surface, releases more sulfur dioxide in this temperature window.

The peaks detected in the middle of the temperature window, between 350 and 650°C, could indicate the decomposition of palladium sulfates. The temperatures for the maximum in these peaks correlate rather well with the light-off temperatures in methane during the fourth test cycle (in the presence of 5 ppm SO₂). Based on this observation it seems that conversion of methane is restricted to the decomposition of palladium sulfates on the surface. The activation energy for methane oxidation is dramatically increased after SO_x poisoning for all Pd catalysts, while Arrhenius pre-

exponential term is relatively constant, indicating a transformation from very active PdO sites to less active PdO–SO_x sites (7). The rather strong SO₂ peaks starting close to 800°C might be due to decomposition of formed aluminum sulfates (of the more stable type) as was discussed earlier. The reason for the lower amounts released from the surface of the Pd–Ba formulation, at high temperatures, compared with the Pd only catalyst, was dealt with above and lies most probably in the fact that sulfur species have reacted with barium oxide forming stable sulfates, which requires higher temperatures to decompose. It is evident that these types of catalysts (Ba promoted) will be saturated by sulfates by time. Therefore it is recommended that the catalyst is subjected to a regeneration procedure using high temperatures and fuel rich conditions (analogous to the NO_x storage concept).

Temperature Programmed Reduction

The CH₄-TPR experiments did not reveal any differences in the reduction temperatures of PdO on (3.0)Pd/alumina and (3.0, 15.0)Pd–Ba/alumina. The consumption of methane takes place at approximately 500°C, above which temperature an increase in the CO signal is observed. Here no promotion effect of Ba on PdO was detected.

CONCLUSIONS

We have shown within this study that, barium, in addition to acting as a hydrothermal promoter in a Pd–Ba/alumina concept, also improves the resistance against sulfur poisoning in biofuel combustion applications and widens the lambda window in NGV applications. The widening of the lambda window was achieved by higher oxidation activities in CO and methane under reducing conditions. Further on we presented a 3-layered catalyst with decreased Pd loading (50% less compared with the reference catalyst), which effectively removed the model reactants (CO, CH₄, and C₁₀H₈) in the presence of sulfur. The believed mechanism was that the sulfur is trapped as sulfates in the barium component leaving PdO active species free for the methane oxidation step. Our conclusions based on the characterization and adsorption studies are summarized as follows:

1. The addition of Ba to a Pd/alumina catalyst improved the palladium dispersion and lowered the mean particle size of the precious metal.
2. XPS measurements indicated that palladium surface concentration was much higher in the barium promoted catalyst.
3. Sulfur is probably oxidized during reaction conditions to form sulfates such as PdSO₄, BaSO₄, and Al₂(SO₄)₃ on the catalysts.
4. Restructuring of the Pd species on the surface of the catalysts seems to take place during the cycled light-off

testing. A change from a single broad peak to a twin-peak in the O₂-TPD patterns of fresh and aged (4 cycles) Pd-Ba/alumina could be an indication of the formation of easily reducible crystalline PdO in addition to the stable amorphous PdO.

5. The differences in the sulfur evolution patterns in the SO₂-TPD experiments over alumina, Ba/alumina, Pd/alumina, and Pd-Ba/alumina were believed to depend on sulfur species, which have reacted with BaO forming ultra stable barium sulfate.

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