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Regeneration of S-poisoned Pd/Al_2O_3 catalysts for the combustion of methane

F. Arosio [a], S. Colussi [b], G. Groppi [a,*], A. Trovarelli [b]

[a] *NEMAS-NanoEngineered Materials and Surfaces Centre Dip. di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, Italy*
[b] *Dip. di Scienze e Tecnologie Chimiche, Università degli Studi di Udine, Italy*

Abstract

Regeneration of S-poisoned Pd/Al_2O_3 catalysts for the abatement of methane emissions from natural gas vehicles was addressed in this work. Investigations were devoted to determine the temperature threshold allowing for catalyst reactivation under different CH_4 containing atmospheres. Under lean combustion conditions in the presence of excess O_2, partial regeneration took place only above 750 °C after decomposition of stable sulphate species adsorbed on the support. Short CH_4-reducing, O_2-free pulses led to partial catalyst reactivation already at 550 °C and to practically complete regeneration at 600 °C. Also in this case reactivation was associated with SO_2 release due to the decomposition of stable support sulphates likely promoted by CH_4 activation onto the reduced metallic Pd surface. Rich combustion pulses with $CH_4/O_2 = 2$ were equally effective to CH_4-reducing pulses in catalyst regeneration.

These results suggest that a regeneration strategy based on periodical natural gas pulses fed to the catalyst by a by-pass line might be efficient in limiting the effects of S-poisoning of palladium catalysts for the abatement of CH_4 emissions from natural gas engine.

Keywords: Pd-catalysts; CH_4 emission abatement; CH_4 combustion; Sulphur poisoning; Catalyst regeneration

1. Introduction

Natural gas represents one promising alternative energy source for the future in automotive and heavy-duty vehicles. In comparison with traditional fuelled vehicles, lean burn natural gas vehicles (NGV) engender a lower impact on environment, thanks to smokeless exhausts and reduced nitrogen oxide emissions due to the lower combustion temperatures associated with the high air to fuel mass ratios (typically 20 or greater) at which the lean engine operates. At given combustion engine efficiency also tailpipe CO_2 emissions in NGV light-duty vehicles can be lower than in conventional fuelled vehicles by virtue of the higher hydrogen-to-carbon ratio of natural gas. Nevertheless, the "green" image of lean burn NGV risks to be compromised by emission of unburned methane, a potent greenhouse gas estimated to have a 20 years global warming potential more than one order of magnitude higher than that of carbon dioxide. Accordingly severe limitations on CH_4 emissions have been enforced [1].

The use of an exhaust oxidation catalyst is the currently adopted way to match CH_4 emission limits, but obstacles arise from the reaction conditions specific to lean burn engines. Typical exhaust gases are characterized by low temperatures (even below 400 °C), presence of water vapour (10–15%), large excess of oxygen and concentration of methane as low as 500–1000 ppm. Under such conditions Pd/alumina catalysts are widely recognized as the most active in combustion of methane [1–4], but suffer from deactivation problems. The loss in activity is mainly attributed to sulphur containing compounds naturally occurring in natural gas or added as odorants necessary for safety reasons, which result in SO_2 concentration of 0.5–1 ppm in exhaust gases [2,5–10].

Several studies focused on the critical effect of SO_2 poisoning on the catalytic oxidation of methane, showing a marked loss in activity related to formation of stable sulphate species [2,5–10] associated with a strong adsorption of SO_3 produced by SO_2 oxidation over palladium catalyst. Several studies evidenced also the influence of the support on the rate of

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* Corresponding author. Tel.: +39 02 2399 3258; fax: +39 02 2399 3318.
E-mail address: gianpiero.groppi@polimi.it (G. Groppi).

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poisoning of the PdO catalyst, deactivation being much faster for non-sulphating support like SiO_2 [11] and SiO_2–ZrO_2 [2] than for sulphating supports, like Al_2O_3 which slow down the deactivation rate by scavenging of sulphate species. On the other hand, catalyst reactivation via decomposition of sulphate species by thermal treatment under oxidizing atmosphere [2,6] or, more effectively, by H_2 reductive conditions [12] was found more difficult for catalyst dispersed over sulphating supports suggesting that decomposition of stable support sulphate species is required for partial or complete reactivation.

In this work, the regeneration of a S-poisoned 2% (w/w) Pd/Al_2O_3 catalyst was investigated by means of alternate pulses and temperature step experiments, in order to evaluate the temperature threshold to obtain catalyst reactivation under different CH_4 containing atmospheres including: lean combustion (excess of O_2); CH_4-reducing (O_2-free) and rich combustion (O_2 deficient) atmospheres. The effect of alternate lean combustion/CH_4-reducing pulses on unpoisoned catalyst was also addressed to better understand modifications of palladium catalyst during reduction/reoxidation cycles.

2. Experimental

Palladium catalysts supported on γ-Al_2O_3 (LaRoche Versal TD250) were obtained by incipient wetness impregnation using an aqueous solution of $Pd(NO_3)_2$ (Aldrich, 10%, w/w, Pd, 99.999%) of the supports calcined at 800 °C for 6 h. 2% (w/w) Pd was loaded in a single impregnation step. Catalysts were dried overnight at 110 °C and then calcined for 6 h at 800 °C in a 0.2 l/min air flow (heating/cooling rate 10 °C/min). The BET surface area of the catalyst was 122 m^2/g.

The fresh catalyst was submitted to accelerated SO_2 poisoning by treatment at 380 °C for 15 h in a stream containing 10 ppm SO_2, 0.5% CH_4, 2% O_2, He to balance at GHSV = 180,000 $cm^3/g/h$ at STP, in the presence of H_2O as a CH_4 combustion product. Details on procedure and poisoning behaviour are reported elsewhere [13].

The performances of fresh and S-poisoned catalysts were studied using a fixed bed tubular quartz micro reactor (i.d. = 7 mm) at atmospheric pressure, placed within an electrically heated furnace. Temperature was monitored by a K-type thermocouple located in the middle of the catalytic bed, consisting of 60 mg of powder catalyst (140–200 mesh) diluted by 60 mg of quartz with the same particle size. Reactant and product compositions including SO_2 and H_2S were monitored by a mass spectrometer with quadrupole detector (Balzers QMS 422). Analyses were periodically verified using a HP6890 GC system.

Different types of experiments were performed to monitor activity of fresh and S-poisoned catalysts.

2.1. Fresh catalyst

Temperature programmed combustion (TPC) tests were carried out feeding the reactor with 0.5% CH_4, 4% O_2, 16% N_2, 2% H_2O, balance He at 150 cm^3/min at STP and GHSV = 150,000 $cm^3/g/h$. H_2O was always co-feed to reactants under all the investigated conditions in view of its well recognized effect on palladium combustion catalyst [14]. Temperature was ramped at 15 °C/min up to two different levels: 500 °C (TPC-500) or 900 °C (TPC-900); respectively, well below and above the threshold of PdO decomposition under the investigated conditions. The catalyst was cooled at the same rate down to room temperature.

Temperature programmed reduction (TPR) experiments were carried out at the same flow rate, GHSV and temperature range conditions with a feed composition of 0.5% CH_4, 2% H_2O, balance He. Temperature was ramped up to 500°C and down to RT at 15 °C/min.

The behaviour of the fresh catalyst at a constant temperature of 350 °C was investigated by the following alternate pulses experiments: (i) a series of alternate lean combustion (0.5% CH_4, 4% O_2, 16% N_2, 2% H_2O, balance He–Ar) and CH_4-reducing (0.5% CH_4, 2% H_2O, balance He–Ar) pulses; (ii) a series of alternate oxidizing (4% O_2, 16% N_2, 2% H_2O, balance He) and CH_4-reducing (0.5% CH_4, 2% H_2O, balance He–Ar) pulses. Alternate pulse experiments were performed according to the following modality. The catalyst was maintained for 30–60 min under lean combustion (or oxidizing) conditions, then the feed was switched to pure He for 40–50 s to favour the desorption of species adsorbed on catalyst surface and the purge of the dead volume. After the purge a reducing stream was fed to the reactor for 2 min. Then a helium purge was again carried out for 40–50 s and finally lean combustion (or CH_4-free oxidizing) conditions were restored. Ar tracer was always fed with CH_4 (CH_4/Ar = 10) to clearly identify the actual switch time between different atmospheres. During all the different phases the flow rate was kept at 150 cm^3/min at STP corresponding to a GHSV = 150,000 $cm^3/g/h$ at STP.

2.2. S-poisoned catalyst

Only TPC-900 test was carried out over S-poisoned catalyst at the same feed composition, flow rate and GHSV adopted for tests over fresh catalyst. Also in TPR the temperature was ramped up to 900 °C.

Three types of temperature step experiments were performed. CH_4 conversion value under lean combustion conditions at 400 °C was initially registered. Temperature was then increased by 50 °C steps at 15 °C/min up to different levels: e.g. 450, 500, 550, 600, 650, 700, 750 and 800 °C. Depending on the type of experiment the following treatments were performed at each temperature step: (i) one hour aging under lean combustion conditions; (ii) a series of four alternate lean combustion/CH_4-reducing pulses according to the same procedure described above; (iii) a series of four alternate lean combustion (0.5% CH_4, 4% O_2, 16% N_2, 2% H_2O, balance He–Ar)/rich combustion (1% CH_4, 0.5% O_2, 2% N_2, 2% H_2O, balance He–Ar) pulses.

After each thermal step the catalyst was cooled down to 400 °C and CH_4 conversion was measured under standard lean combustion conditions so to evaluate activity differences by comparison with the conversion determined at the beginning of the experiment.