Propene induced reversible deactivation effects in diesel oxidation catalysts

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ABSTRACT

By applying different transient test protocols in a lab reactor, it is demonstrated that in the presence of C_3H_6 a Pt/Pd based oxidation catalyst experiences a persistent deactivation that can be attributed to the accumulation of propene partial oxidation products on the catalyst surface. The deactivation can be reversed by treating the catalyst at higher temperature in a hydrocarbon free atmosphere. The three most important scenarios giving rise to the activation/deactivation phenomenon are:

(1) Consecutive heat-up/cool-down cycles: If several consecutive heat-up/cool-down cycles are performed with a catalyst pretreated in a propene free oxidative atmosphere, a lower ignition temperature is observed during the first heating ramp than during the following cycles. The effect can be explained by a reversible blocking of active sites by hydrocarbon (HC) intermediates, which are formed during the ignition branch, then entirely are removed after the HC ignition is completed and finally are formed again during the extinction branch, providing a deactivated state of the catalyst for the following ignition. The deactivation can be completely reversed either by a conditioning in an oxidizing HC free gas mixture at temperatures above 110 °C or a conditioning in N_2 above 140 °C. The deactivation effect is more pronounced under conditions that lead to a low light-off temperature and completely disappears at conditions leading to higher light-off temperatures, i.e. high CO concentrations or high space velocities.

(2) Light-off tests with varying temperature ramp rate: For faster ramp rates, CO/propene ignition is observed at lower inlet temperatures. This is the opposite behavior than would be expected based on thermal considerations and can be explained by a higher accumulation of HC intermediates during the slower ramp.

(3) Transient observation of the deactivation effect: If an initially clean catalyst is operated at a constant temperature in the light-off range, a transient decrease in CO/HC conversion is observed that can be attributed to the gradual build-up of the blocking HC intermediates.

A kinetic model is presented which considers not only the standard CO and hydrocarbon oxidation kinetics, but also the formation of site blocking intermediates by partial oxidation of propene and the removal of these blocking intermediates either by total oxidation with O_2 or by thermal desorption. The model nearly quantitatively reproduces the experimental results of the different test protocols.

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1. Introduction

The diesel oxidation catalyst (DOC) is a key component in diesel exhaust gas aftertreatment systems for the oxidation of hydrocarbons (HC) and CO as well as for the conversion of NO to a desired NO_2/NO ratio. Typical catalysts are Pt or a combination of Pt and Pd [1,2].

It has been reported [3–10] that under typical exhaust treatment operating conditions reversible activation and deactivation, as well as irreversible deactivation effects can be observed. This artifact poses a fundamental challenge for the assessment of the catalyst performance as well as for the application of global kinetic models in reactor simulations. Global kinetic models are usually empirical and have a form similar to the Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate expressions (although they are not derived using the classical LHHW approach) [11]. For comparisons of different catalyst technologies, as well as for the parametrization of global kinetic models, steady state experiments (or very slow

transient ones) are typically applied [1,2,12,13]. Both procedures rely on the assumption that the rates of the surface reactions are only controlled by competition for surface sites and that steady state surface concentrations are instantly established for given gas phase conditions [14,15]. Thus global rate laws can be formulated and catalytic performance can be assessed as a function of only the current gas phase concentrations and the surface temperature, and not the recent history of operating conditions.

One prominent example for such a reversible activation/deactivation effect is the inverse hysteresis during NO oxidation investigated by Hauptmann et al. [5]. on a Pt catalyst. The effect was explained as a reversible oxidation of the catalyst surface by NO_2 or O_2 at higher temperatures and a reduction of the oxides by NO at lower temperatures. The inverse hysteresis effect has been investigated in more detail in a number of studies [6–9] and can be reproduced by global [7,9] as well as by microkinetic models [5] for simple gas mixtures.

Dubbe et al. [9] recently reported, apart from the inverse NO hysteresis on platinum, further deactivation and reactivation effects in CO, NO and C_3H_6 conversion on platinum as well as on palladium catalysts which were attributed to a reversible oxidation/reduction of the precious metal.

The practical relevance of such reversible activation/deactivation effects has been highlighted by Bantl-Konrad et al. [15] and Arvajová et al. [10] for the adjustment of an optimal NO/NO_2 ratio.

Investigating the oxidation of CO/C_3H_6 mixtures during a single ignition/extinction experiment, Abedi at al [16]. observed a switch from a normal to an inverse hysteresis with decreasing CO/C_3H_6 ratio. By using DRIFT-spectroscopy on Pt/Al_2O_3 powder samples to analyze surface species, the effect was attributed to the formation of HC residuals competing with other pollutants for active sites. Herrmann et al. [14] extended the work of Abedi et al., and measured the CO and C_3H_6 conversion during consecutive ignition extinction experiments on a similar catalyst. They concluded that the inverse hysteresis observed by Abedi et al. was not, in fact, a hysteresis effect but rather a permanent deactivation which could be reversed by a temperature ramp up to 350 °C in a flowing gas without pollutants. Hazlet and Eppling reported that in gas mixtures containing CO and propene after the initial onset of CO conversion a plateau in the CO light-off curve is observed before full conversion is reached at higher temperatures [17]. It was shown by DRIFTS experiments that this observation can also be explained by an inhibition of the catalyst by partial oxidation products of propene [17] [18].

In this work we investigate the deactivation and reactivation effects of a Pt/Pd catalyst in greater detail than were investigated on the Pt catalysts. Therefore we perform consecutive ignition extinction experiments, show for which temperature range of the heat-up/cool-down sequence HC intermediates are formed and removed, and investigate which temperatures are necessary to reactivate the catalyst either in oxidative gas mixtures free of pollutants due to reaction or in N_2 due to desorption of HC intermediates. Besides this, we demonstrate that the applied heating ramp of an ignition experiment significantly effects the conversion curves, corresponding to different degrees of deactivation, and make statements about various deactivation states obtained under different reaction conditions.

Finally, a macro kinetic single channel model that takes into account the formation and removal of HC intermediates is formulated. The purpose of the modeling work is to show that the observed deactivation phenomenon can be quantitatively explained by the assumption of the formation and the removal of HC intermediates during the ignition extinction cycle and to illustrate the effects.

2. Materials and methods

2.1. Experimental

2.1.1. Catalyst and reactor

A monolithic Pt/Pd diesel oxidation catalyst (length: 7.62 cm, diameter: 2.54 cm, 400 cpsi, 4 mil (0.1016 mm) wall thickness, hydrothermally aged (750 °C for 5 h), noble metal loading 125 g/ft^3, Pt/Pd ratio 3:1 (kg/kg)) was used for all experiments. The monolith was wrapped with insulation and placed in a stainless steel tubular reactor taking care to ensure that no gas bypass of the monolith occurred.

2.1.2. Apparatus

The flow system consisted of a gas mixing unit, a gas pre-heater with the reactor and an analyzer module. Mass flow controllers were used to control and monitor the flow rate of each gas species. For experiments with water, steam was dosed to the feed using an evaporator system. Before passing through the monolith the gas mixture was heated in a tubular furnace. To ensure a uniform temperature profile and to enhance mixing of the gases, static mixers were installed in the oven. A k-type thermocouple was placed 1.5 cm in front of the catalyst entrance to monitor temperature.

2.1.3. Analyzer

NO and NO_X at the reactor outlet were analyzed using a chemiluminescence detector (CLD) and a flame ionization detector (FID) was used for the hydrocarbons assay. A paramagnetic method (MLT) was utilized to monitor O_2, while CO and CO_2 were analyzed applying a non-dispersive infrared sensor (NDIR).

2.1.4. Pretreatment

Before each experiment was performed the catalyst was treated with a defined mixture of inert gas species (10 % CO_2, 10 % H_2O, 10 % O_2, N_2 balance gas) while a temperature ramp from 75 to 400 °C and then back to 75 °C with a heating rate of 40 K/min and a cooling rate of −20 K/min was employed. The holding time at 400 °C was 5 min.

2.1.5. Ignition/extinction experiments

After the pretreatment, several ignition-extinction (IE) experiments were performed. The preheated gas stream with the inert gas species (10 % O_2, 10 % CO_2 and 10 % H_2O, N_2 balance gas) was mixed with a defined amount of noxious gases at a defined GHSV (STP) before reaching the catalyst. The ramp's maximum temperature is mentioned in the figure captions. The applied noxious gas concentrations, the ramp rates as well as the space velocities are reported in Table 1 for all types of experiments.

2.2. Simulation

Simulations were performed with a model that solves the heat and mass balance equations for a single catalyst channel. The balance equations for the gas phase were solved in terms of velocity averaged concentrations and temperature. Heat and mass transfer from the gas phase to the wall were described by heat and mass transfer coefficients computed from a Nusselt number correlation. Diffusion resistances in the washcoat were not explicitly solved for so that they are implicitly contained in the kinetic parameters. A detailed description if the applied simulation model can be found in Hauptmann et al. [19].