HC-Induced Deactivation in CO Conversion at Diesel Oxidation Catalysts

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Received: 22 September 2015 / Revised: 28 June 2016 / Accepted: 11 July 2016 / Published online: 8 August 2016
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Abstract This paper examines the activity of a platinum catalyst for the oxidation of CO under conditions of temperature cycling. Each cycle consists of an ignition and extinction curve obtained with a linear temperature ramp. It is shown that the catalyst activity is higher for the first ignition cycle than for the subsequent ones regarding CO conversion. The activity for the extinction portion of each cycle is the same for all cycles. It is proposed that the loss of catalyst activity results from the deposition of hydrocarbon residues during the extinction part of the cycle. The catalyst activity can be completely restored by heating the catalyst to 350 °C in the presence of oxygen and nitrogen.

Keywords Diesel oxidation catalyst · Deactivation · Reactivation · HC intermediates · Inverse hysteresis

1 Introduction

To date, most simulation work on exhaust treatment systems is based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach, i.e., it is assumed that the rates of the surface reactions are controlled by competition for surface sites and that steady state surface concentrations are instantly

established for given gas phase conditions [1]. One important consequence arising from these assumptions is that global rate laws can be formulated, which describe the observed rates r as a function of only the current gas phase concentrations and the surface temperature $r(c_{\text{gas}}, T)$, and not the history of operating conditions.

It has been pointed out [2–10] that under typical exhaust treatment operating conditions, reversible activation/deactivation effects can be observed. This is a fundamental challenge for the currently established LHHW-based modeling approach since, in the presence of the activation/deactivation effects, the observed reaction rate becomes a function of the recent catalyst history.

One prominent example for such a reversible activation/deactivation effect is the inverse hysteresis during NO oxidation observed by Hauptmann et al. [2]. The effect can be explained by a reversible oxidation of the platinum surface by NO₂ or O₂ at higher temperatures and a reduction of the platinum oxides by NO at lower temperatures. The inverse hysteresis effect has been investigated in more detail in a number of studies [4–7], and it has been shown that for simple gas mixtures, the hysteresis behavior can be quantitatively reproduced by global [5–7] as well as microkinetic models [2]. Apart from the inverse NO hysteresis on platinum, further deactivation and reactivation effects caused by different precious metal oxidation states were reported for NO, CO, and propene conversion on platinum as well as on palladium by Dubbe et al. [7]. They assessed the reducing potential of single pollutants and pollutant's gas mixtures, proposed a modeling approach, and simulated the effects in the case for NO for both noble metals.

The practical relevance of such reversible activation/deactivation effects for the adjustment of an optimal NO/NO₂ ratio has been highlighted by Bandl-Konrad et al. [10] and Arvajová et al. [11]. They showed that a reducing CO and

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C₃H₆ pulse can restore the activity of deactivated PtO_x while keeping lean conditions.

A similar inverse hysteresis effect has recently been reported by Abedi et al. [3] for the oxidation of hydrocarbon/CO mixtures. It was observed that during a heat-up/cool-down sequence, the CO/H₂ ignition occurred at lower temperature than the corresponding extinction. Using DRIFT-spectroscopy on Pt/Al₂O₃ powder samples, the effect was attributed to the formation of HC intermediates competing with CO for active sites.

In this work, we further investigate the activation/deactivation effect reported by Abedi et al. [3]. By following the CO conversion during several consecutive light-off experiments, the origins of this effect are examined. We also study the reversibility of the deactivation process. Furthermore, we systematically investigate the impact of the pretreatment on the catalyst's activity.

2 Materials and Methods

2.1 Apparatus

The apparatus used in this work consisted of a gas mixing unit, a gas preheater with a 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.

2.2 Catalyst and Reactor

A monolithic diesel oxidation model catalyst (Umicore AG & Co. KG, Pt/Al₂O₃, length 7.62 cm, diameter 2.54 cm, 400 cpsi, 4.33 mil wall thickness, hydrothermally aged (600 °C for 10 h), noble metal loading 80 g/ft³) was used for all experiments. The monolith was wrapped with insulation and placed in a stainless steel tubular reactor taking care to ensure no gas bypass of the monolith occurred.

2.3 Temperature

Temperature profiles were monitored using four K-type thermocouples. One was placed 0.5 mm in front of the catalyst, two in central channels (0.5 and 55 mm behind the inlet), and one 10 mm behind the outlet. For reason that the two thermocouples inside the catalyst block fewer than 1 % of the channels, the impact on the flow field is assumed to be negligible. For reference purposes, the temperature measured 0.5 mm in front of the catalyst's entrance is used.

2.4 Analyzer

NO and NO_x at the reactor outlet were analyzed using a chemiluminescence detector (CLD). Whereas a flame ionization detector (FID) was applied for the hydrocarbons assay. For the CO monitoring, an IRD measurement was utilized, which is based on heat generation by infrared radiation passing a cuvette filled with the sample.

2.5 Pretreatment

Before each experiment was performed, the catalyst was treated with a defined mixture of inert gas species (see Table 1) while a temperature ramp from 80 to 350 °C and back to 80 °C with a heating rate of 8 K/min was employed.

2.6 Light-Off/Light-Down Experiments

After the pretreatment, several light-off/light-down experiments were performed. The ramp reached from 80 to 350 °C and back to 80 °C with a heating rate of 8 K/min. The preheated gas stream with the inert gas species (6 % O₂, 11 % CO₂, and 8 % H₂O, N₂ balance gas) was mixed with 350 ppm CO, 120 ppm H₂, 100 ppm C₃H₆, 50 ppm C₃H₈, and 270 ppm NO at a space velocity of 25,000 h⁻¹ before reaching the catalyst.

3 Results and Discussion

3.1 Hysteresis at the Pt-Catalyst

Two consecutive ignition/extinction experiments were performed using the temperature ramp scheme shown in Fig. 1a. The three ramps represent the conditioning ramp and the subsequent two ignition/extinction experiments. The conversion of the pollutant CO, total hydrocarbons, and NO during these experiments is shown in Fig. 1b–c.

Figure 1b shows the CO ignition and extinction curves. The second light-off curve describing the conversion of CO to CO₂ is shifted to a higher temperature of approximately 20 K compared to the first one. The light-down curves are, however, congruent for both experiments and lay between the

Table 1 Gas species for the different pretreatments of the catalyst

Pretreatment	N ₂	CO ₂ /%	O ₂ /%	H ₂ O/%
N ₂ /CO ₂	Balance gas	11	–	–
N ₂ /CO ₂ /O ₂	Balance gas	11	6	–
N ₂ /CO ₂ /H ₂ O	Balance gas	11	–	8
N ₂ /CO ₂ /H ₂ O/O ₂	Balance gas	11	6	8

Fig. 1 **a** Schematic temperature ramp for a conditioning phase in N_2 , CO_2 , and O_2 and subsequent two ignition/extinction experiments for 350 ppm CO, 270 ppm NO, 100 ppm propene, 120 ppm H_2 , 50 ppm C_3H_8 , 6 % O_2 , 11 % CO_2 , 8 % H_2O and N_2 balance gas at a space velocity of $25,000\ h^{-1}$. The conversion of CO, NO, and HC during the experiments is depicted in **b–d**. The *solid lines* represent the ignition branches and the *dashed lines* the extinction

first and the second light-off. Obviously, a deactivation takes place after or during the first light-off which leads to an inverse hysteresis for the first ramp and normal hysteresis for the second ramp.

In contrast to the conversion of CO to CO_2 , the two light-off curves of the NO oxidation do not show significant differences (Fig. 1c). However, NO conversion consequently shows a poorer performance during the extinction than during the ignition, which is a strong evidence for a reversible deactivation that takes place at high temperatures and is reversed at low temperatures. Around 300 °C, the CLD detecting NO shows a slightly higher conversion than the expected one according to the thermodynamical equilibrium. This deviation can be explained by inaccuracies in the assay.

For the total hydrocarbon oxidation (Fig. 1d), both ignition and extinction branches show substantial oscillations. However, the ignition and extinction temperature can be determined and strong hysteresis phenomena can be excluded. Indeed, the propene is completely oxidized by 350 °C, whereas very little propane is converted up to 350 °C.

Although deactivation phenomena can be observed in NO and CO conversion during the consecutive ignition/extinction experiments, their impacts on the pollutant conversions are different. While an inverse hysteresis is constantly observed in the case of NO during the heating/cooling cycles, the CO conversion features a switch from an inverse hysteresis during the first cycle to a normal hysteresis during the second cycle.

The phenomenon of a constant inverse hysteresis in NO conversion can be explained by Pt oxide formation with formed NO_2 and/or O_2 at high temperatures and a reduction of the active species by NO, CO, or HC species at low temperatures [2, 5, 7].

However, the effect of a switch from a normal hysteresis to an inverse hysteresis in CO conversion during consecutive light-off/light-down experiments has not been reported so far and will be investigated in detail in the following sections.

3.2 Deactivation in CO Oxidation

Three consecutive ignition/extinction experiments were then performed using the temperature ramp scheme shown in Fig. 2a. The four ramps represent the conditioning ramp and the subsequent three ignition/extinction experiments.

Figure 2b shows the ignition curves of these experiments. The conversion of CO to CO_2 shifts to a temperature approximately 20 K higher after the first ignition. A deactivation takes place. The ignition and extinction temperature remain constant for the deactivated catalyst during all following light-off/light-down cycles. The deactivation is irreversible under the applied conditions.

It seems to be illogical that such an effect is caused only by noble metal oxidation because under these circumstances, the catalyst should not be in the most active state after a conditioning phase in an oxidative environment. A reduction of

Fig. 2 **a** Schematic temperature ramp for a conditioning phase in N_2 , CO_2 , and O_2 and subsequent three ignition/extinction experiments for 350 ppm CO in 270 ppm NO, 100 ppm propene, 120 ppm H_2 , 50 ppm C_3H_8 , 6 % O_2 , 11 % CO_2 , 8 % H_2O and N_2 balance gas at a space velocity of $25,000\ h^{-1}$. The conversion of CO during the first, second, and third ignition is depicted in **b**

noble metal, which can be caused by NO or other reducing species at low temperatures would probably result in an activated catalyst at the beginning of each light-off experiment. We do not claim that noble metal oxidation does not influence the CO ignition curve, which has already been reported by Hauptmann et al. and by Dubbe et al. [5, 7]. However, we do claim that it is unlikely that the reported effect in this work is only caused by the formation of PtO_x .

Another deactivation phenomenon is the formation of HC intermediates, which can occur during the C_3H_6 ignition. In this context, Abedi et al. have investigated the oxidation of CO/ C_3H_6 mixtures at Pt/Al_2O_3 and reported a switch from a normal to an inverse hysteresis for both pollutants with decreasing CO/ C_3H_6 ratio [3]. They not only observed this effect but also detected the HC intermediates applying DRIFT-spectroscopy.

3.3 What Is the Reason for the Deactivation?

To verify if the deactivation in CO conversion is caused by the formation of HC intermediates or rather by other deactivation mechanisms, two consecutive ignition/extinction experiments were performed in the absence of hydrocarbons after a conditioning phase according to the ramping protocol shown in

Fig. 3a. Unlike the previous experiments, the conditioning gas contained hydrocarbons and was equal to the deactivating gas mixture used for the ignition/extinction experiments in Figs. 1 and 2. The CO conversion during the first and the second ignition branch is depicted in Fig. 3b.

The CO ignition curve, which was obtained directly after the conditioning phase in the gas mixture containing hydrocarbons, is shifted to a higher temperature of approximately 20 K at 50 % conversion compared to the second ignition curve. Thus, a reversed trend can be observed for this experiment compared to the two previous ones. At this state, it seems logical to assume that the deactivation is somehow caused by hydrocarbons because the conditioning in their presence deactivated the catalyst. Further, the experiment's results provide strong evidence that the deactivation is not permanent because the catalyst reaches a more active state after a light-off/light-down cycle in the absence of hydrocarbons. Obviously, a reactivation takes place which will be investigated in detail in the following sections.

3.4 Reactivation of the Catalyst

If a temperature ramp up to 350 °C is applied in the absence of pollutants, the deactivation can completely be reversed. To examine the reactivation of the catalyst, a sequence of light-off/light-down experiments was performed using the ramping protocol shown in Fig. 4a. The catalyst was conditioned in $N_2/O_2/CO_2$, and three ignition/extinction experiments were performed. Following this, the catalyst was again conditioned and three more ignition/extinction experiments were conducted. Figure 4b shows the first, second, and third ignition curve obtained after the conditioning. The corresponding temperatures for 50 % CO conversion are presented in Fig. 5.

An activated light-off can be observed after the first and the second conditioning phase which shows 50 % conversion at 130 °C. The following extinctions occur at approximately 13 K higher temperature (see Fig. 5). The subsequent light-offs require approximately 150 °C for 50 % CO conversion, whereas the extinction curves had 50 % conversion at 143 °C, the same as the first extinction. If we attribute the effect to the formed HC intermediates investigated by Abdei et al. [3], it seems to be logical that the intermediates are formed after the first ignition (during the first propene light-off). They lead to a deactivation of the platinum which remains constant for following light-offs and light-downs. The differences in ignition and extinction temperature at the deactivated catalyst can be explained by effects such as thermal inertia or multiple steady states [2]. An applied temperature ramp up to 350 °C in the absence of pollutants is sufficient to remove all of the intermediates resulting in a re-activation of the platinum.

We can speculate on when during the cycle of ignition and extinction the hydrocarbon intermediates are formed. It is reasonable to assume that the intermediates are formed and

Fig. 3 b Conversion of 350 ppm CO during two consecutive ignition/extinction experiments in 270 ppm NO, 120 ppm H₂, 6 % O₂, 11 % CO₂, 8 % H₂O and N₂ balance gas at a space velocity of 25,000 h⁻¹ after a conditioning phase in the same gas mixture with the addition of 100 ppm C₃H₆ and 50 ppm C₃H₈. A schematic temperature ramp for the procedure can be seen in **a**

remain stable on the surface more readily at lower temperatures. Thus, they would be formed at the earlier stages of the ignition curve and would affect the ignition of all experiments equally. It is also likely that the intermediates are formed from propene and not from propane owing to the fact that propane shows nearly no conversion under the applied conditions. For a fresh catalyst with a clean surface, hydrocarbon intermediates probably do not form until the oxidation of CO is

complete, since the surface of the fresh catalyst is mostly covered by adsorbed CO [12]. After 100 % conversion is reached, at higher temperature, it is less likely that there would be HC residues left on the surface. At temperatures well above the light-off, all the C₃H₆ will be converted within the first millimeters of the channel, so that most of the catalyst is subjected to an HC-free gas mixture that is very similar to the gas mixture applied during catalyst regeneration. It can therefore be assumed that at high temperatures, most of the catalyst is free of HC residues. It has been observed that the light-off initially occurs at the catalyst exit, and the reaction front progresses to the entrance [13]. For the extinction front, a reverse behavior is expected, that is, the extinction front moves in the flow direction from the reactor entrance to the exit. We therefore suggest that the HC residues are deposited during the extinction phase of the cycle and are laid down progressively as the extinction progresses. These residues would thus be present and inhibit the CO oxidation during the next ignition cycle. If the HC intermediates are all removed by the end of the ignition phase, then the next extinction portion would lay down new intermediates in an equivalent manner to the first ignition phase, and thus there would be no accumulation of the intermediates on the surface. Thus, all subsequent ignition cycles would be the same, which is consistent with the observed behavior.

Fig. 4 a Schematic temperature ramping sequence for a conditioning phase and subsequent three ignition/extinction experiments, conducted twice. The conditioning ramp was performed in N₂, CO₂, and O₂, and the ignition/extinction experiments were conducted in 350 ppm CO, 270 ppm NO, 100 ppm Propene, 120 ppm H₂, 50 ppm C₃H₈, 6 % O₂, 11 % CO₂, 8 % H₂O and N₂ balance gas at a space velocity of 25,000 h⁻¹. The conversion of CO during the first, second, third/fourth, fifth, and sixth ignition is depicted in **b**

Fig. 5 Required temperature for 50 % CO conversion in the presence of C₃H₆ during ignition (blue) and extinction (red) for the first, second, and third ramp after a pretreatment in N₂, CO₂, and O₂

Table 2 Required temperature for 50 % CO conversion in the presence of C_3H_6 for the first, second, and third light-off (LO), with different pretreatments of the catalyst preceding the first LO

Pretreatment	$T_{50\%}$ first LO/ $^{\circ}C$	$T_{50\%}$ second LO/ $^{\circ}C$	$T_{50\%}$ third LO/ $^{\circ}C$
N_2/CO_2	137	149	149
$N_2/CO_2/O_2$	130	151	152
$N_2/CO_2/H_2O$	131	147	148
$N_2/CO_2/H_2O/O_2$	125	148	148

3.5 Influence of the Pretreatment

The required temperatures for 50 % CO conversion of the first, second, and third ignition after different pretreatments are shown in Table 2. Before each pretreatment was carried out, the catalyst was in a deactivated state. A depiction of the results in Table 2 is provided in Fig. 6. The results show that the catalyst's pretreatment strongly affects its activity. The addition of water or oxygen as a single component to N_2/CO_2 during the pretreatment lowers the first ignition temperature by approximately 7 K compared to the original pretreatment. The addition of both species water and O_2 even results in 12 K ignition point depression. The deactivated catalyst always shows an ignition temperature ($T_{50\%}$) of approximately 150 $^{\circ}C$.

The fact that a pretreatment in the absence of H_2O and O_2 leads to an incomplete re-activation might be a hint that different mechanisms are responsible for the removal of HC intermediates. While probably only desorption processes occur in a gas mixture of N_2 and CO_2 , the addition of oxygen

obviously results in an HC-intermediate oxidation, whereas H_2O could be a reactant for a steam reforming reaction. The idea of different reactivation mechanisms is underpinned by the fact that the combination of H_2O and O_2 as reactivating gas mixture leads to a higher degree of reactivation compared to the single components. Thus, one could speculate that there might be three different types of HC intermediates, which can be removed from the catalyst surface either by desorption, oxidation, or the steam reforming reaction.

4 Conclusions

The CO conversion during the oxidation of CO/HC mixtures with oxygen on platinum was studied in consecutive heat-up/cool-down cycles. It was shown that during the first heat-up cycle on a clean catalyst surface, a lower light-off temperature is observed than during the following cycles. The effect can be explained by a reversible blocking of active sites by HC residues. This deactivation can be reversed by a heat-up/cool-down cycle with an oxidizing exhaust mixture not containing any HC. A complete reactivation is obtained with mixtures that contain O_2 and/or H_2O , while a mixture of CO_2 and N_2 yields only a partial regeneration.

The effect presented in this paper is a further example of a reversible activation/deactivation effect that occurs under typical exhaust aftertreatment operating conditions. Such activation/deactivation effects pose a significant challenge for simulation of exhaust aftertreatment devices, since current simulation approaches are mostly based on the assumption of steady state surface conditions, i.e., it is assumed that the

Fig. 6 Required temperature for 50 % CO conversion in the presence of C_3H_6 for the first, second, and third light-off after a pretreatment in **a** N_2/CO_2 , **b** $N_2/CO_2/O_2$, **c** $N_2/CO_2/H_2O$, and **d** $N_2/CO_2/H_2O/O_2$

kinetics can be described by a rate law as a function of only the current gas concentrations and surface temperatures with no influence of the recent catalyst operation history.

Ultimately, the goal is to obtain a mechanistic understanding of the different activation/deactivation effects and to include a physical description of the effects in the simulation models. However, given the number and complexity of the effects, the derivation of a quantitative model description of them is a major challenge.

A sound understanding of the different activation/deactivation behavior is also needed if the effects are not explicitly simulated, since, in this case, the models will implicitly represent a certain activation state that is determined by the test sequence applied for model calibration. Therefore, it is important that the test protocols represent realistic operating conditions also with respect to the activation/deactivation effects. Concerning the deactivation effect discussed in this paper, this means that if light-off tests are applied for model calibration, a realistic preconditioning needs to be ensured before each light-off test to ensure that the desired initial catalyst surface condition is achieved.

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