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De- and Reactivation Behaviour of Pt/Pd Diesel Oxidation Catalysts

Recent findings regarding the conversion behaviour of diesel oxidation catalysts reveal that the conversion of noxious substances can severely differ, depending on the oxidation state of the catalyst, which is strongly dependent on temperature. In an FVV cooperation project between the Institute of Chemical Process Engineering of the University of Stuttgart and the Institute of Chemical Technology at the Karlsruhe Institute of Technology, detailed studies have been conducted on the oxidation of platinum- and palladium-based diesel oxidation catalysts. New insights into both particle morphology and the appropriate macrokinetic modelling of the diesel oxidation catalyst conversion behaviour have been gained and will be discussed briefly.



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1	MOTIVATION
2	EXPERIMENTAL APPROACH
3	MACROKINETIC MODELLING
4	PARTICLE MORPHOLOGY OF THE ALLOYED CATALYST
5	CATALYST AGING
6	SUMMARY

1 MOTIVATION

The interest in global kinetic models of exhaust gas aftertreatment reactions is steadily increasing, in order to adequately estimate the conversion behaviour for online control purposes as well as to offline develop optimised operation strategies. In [1] the de- and reactivation in the NO oxidation behaviour of Pt-only catalysts were described and the findings were attributed to a reversible oxidation and reduction of the noble metal. Based on this work, in [2] a macrokinetic model for the NO oxidation was developed and validated using light-off/light-out experiments [2]. This was the starting point of the research project (see [3]) which will be presented in the following, aiming at:

- extension of the existing NO oxidation model to the oxidation of additional noxious substances like CO and unburnt hydrocarbons (HCs)
- transfer of the model from Pt to palladium based and Pt/Pd-alloyed catalysts
- physical and chemical characterisation of the alloyed catalyst in the fresh and aged state.

2 EXPERIMENTAL APPROACH

Near-series model diesel oxidation catalysts (DOC) have been supplied by Umicore with Pt and Pd as active component (80 g_{Me}/ft³-Al₂O₃, 400 cpsi, wall thickness 0.1651 mm (6.5 mil)). Since all catalysts are from the same production batch, good comparability of the results is assured. The mass ratio of the Pt/Pd-alloyed catalyst was Pt:Pd = 2:1 which corresponds to an atomic frac-

tion of approximately 1:1. The experimental data presented in the next section have been measured in an isothermal flat-bed reactor [4] at ICVT. Catalyst samples of one channel height were dissected from the monoliths and placed inside the reactor. Subsequent light-off/light-out measurements were conducted according to the following procedure:

- reducing pre-treatment: (3 % H₂ in N₂, 1 h, 350 °C)
 - permanent feed: CO₂ (7 %), O₂ (5 %), H₂O (5 %) and N₂ (balance)
 - space velocity: 40.000 h⁻¹
 - temperature ramp speed: ±3 K/min between 60 and 400 °C.
- The feed concentrations of CO, NO and propene (as HC-representative) were varied.

3 MACROKINETIC MODELLING

The system behaviour is described using a one-dimensional convection-diffusion model, assuming ideal gas behaviour and axially isothermal conditions. This leads to a quasi-stationary material balance for each component *j* in both gas and surface phase. An additional balance has been added to describe the space- and time-dependent fraction $\theta_{Me}(z,t)$ of the reduced noble metal. It is assumed, that the oxidised form of the noble metal ($1 - \theta_{Me}$) is less active than the reduced form. For the NO-, CO-, and the propene-oxidation, two reaction rates for the reduced and for the oxidised state of the catalyst have been postulated and parametrised (r_i^{Me} respectively r_i^{MeO}). The total rate of the respective reaction is then calculated by weighted interpolation with the fraction $\theta_{Me}(z,t)$ of reduced noble metal:

$$\text{Eq. 1} \quad r_i^{ges}(z,t) = r_i^{Me}(z) \cdot \theta_{Me}(z,t) + r_i^{MeO}(z) \cdot (1 - \theta_{Me}(z,t))$$

As shown previously [1, 2], Pt-based catalysts are oxidised by diesel exhaust above 300 °C, which leads to reversible deactivation. This oxide can be thermally decomposed at temperatures higher than 350 °C. A second path of reactivation is the Platinum-oxide reduction at low temperatures in the presence of NO, CO, or C₃H₆ in the feed. If, as in the tests, the temperature is ramped (at 3 K/min) between 60 and 400 °C, the conversion rates shown in **FIGURE 1** are obtained for non-aged catalysts. With a feed of 800 ppm CO and 500 ppm NO, Pt-only results in the hysteresis of NO oxidation as shown in **FIGURE 1** (left). Starting from low tem-

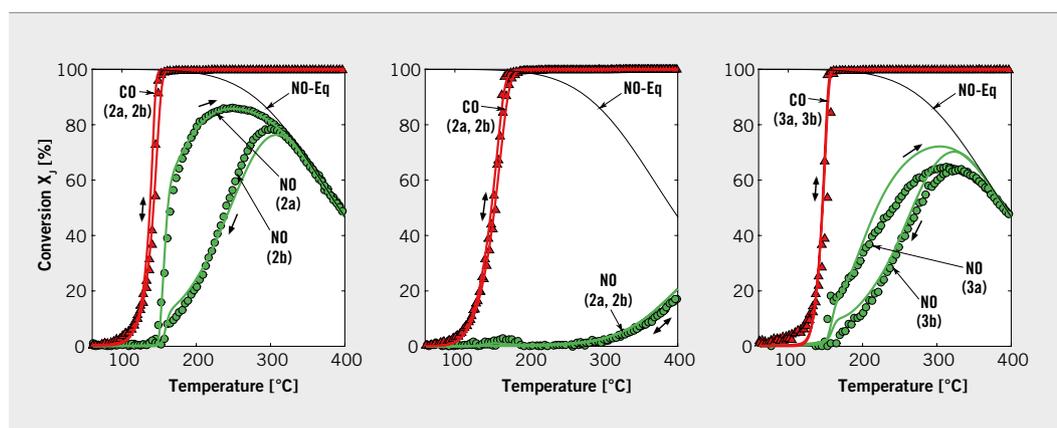


FIGURE 1 Experimental and simulation results with feed 800 ppm CO and 500 ppm NO (2nd cycle Pt-only (left), 2nd cycle Pd-only (centre) and 3rd cycle Pt/Pd (right) in the fresh (non-aged) state; the quasi-stationary cycle is presented (© ICVT)

peratures, the NO conversion is initially high on the reduced Pt and decreases with rising temperature due to noble metal oxide formation and thermodynamic limitation (NO-equilibrium conversion shown as NO-Eq). During subsequent light-out the NO conversion is now significantly lower on the oxidised Pt which leads to the presented hysteresis. On the Pd-only catalyst, **FIGURE 1** (centre), no hysteresis is observed for either NO or CO conversion and the NO overall conversion is expectedly low. In contrast, on the Pt/Pd-alloyed catalyst, a persistent hysteresis in the NO conversion can again be observed, **FIGURE 1** (right).

As mentioned, the conversion branches in **FIGURE 1** are always taken from the settled (quasi-stationary) cycle of the respective catalyst. The Pd-only catalyst already reaches this stable state after one light-off/light-out cycle. Only a slight reduction of the oxide by CO and hence a, for application purposes negligible, reactivation is observed. On the alloyed catalyst, the hysteresis phenomena mostly vanish if all three noxious substances are present in the feed. **FIGURE 1** shows a good agreement between experimental data and simulation results on all three catalysts in the fresh (non-aged) state. Especially the interaction with CO and HC is appropriately described.

4 PARTICLE MORPHOLOGY OF THE ALLOYED CATALYST

A physical and chemical characterisation of the alloyed catalyst has been conducted at the ITCP. The main result was, that the Pt/Pd alloy mostly tends to be distributed very heterogeneously. It was observed, that the alloy composition varies extremely strong on particles with a diameter smaller than 5 nm and small particles seem to have a higher Pd content compared to larger ones. Even Pd-only particles were detected whereas no Pt-only was found. Furthermore, on larger particles a core-shell structure was observed where a Pt-rich core is surrounded by a Pt/Pd alloy shell with variable composition. The integral particle mixture of the alloyed catalyst was measured using HAADF-STEM and EDXS analysis and is depicted in **FIGURE 2**.

5 CATALYST AGING

For application purposes the catalyst needs to be described over its total life-cycle including deactivation due to catalyst aging. In order to test the applicability of the model on aged catalysts, samples have been thermally treated in a muffle furnace at different temperatures (700 and 750 °C, 16 h, lean atmosphere). Afterwards, light-off/light-out experiments have been conducted according to section 3. Also, CO chemisorption experiments were performed at ITCP in order to estimate the noble metal dispersion. As a first step, the applicability of the aging correlation described in [5] for Pt-only catalysts was tested for all three catalysts. Based on this publication, the dispersion D (the share of noble metal atoms in the total amount of noble metal) after an aging duration of t hours at a temperature T can be calculated as follows:

$$\text{Eq. 2} \quad D(t,T) = \alpha(T) + [1 - \alpha(T)] \cdot e^{-dt}$$

$$\text{Eq. 3} \quad \alpha(T) = a + bT + cT^2$$

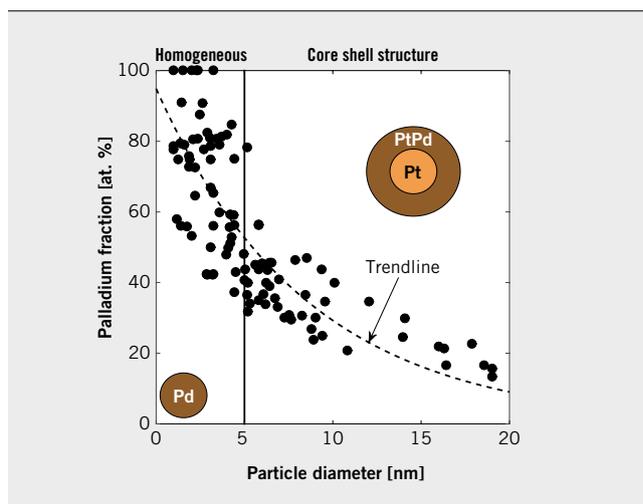


FIGURE 2 Integral particle composition of the alloyed catalyst (HAADF-STEM und EDXS investigation of 100 particles [3]) (© KIT | ICVT)

Here, a, b, c and d are model parameters that particularly depend on the noble metal. For the Pt-only catalyst, the correlation leads to very good results. With some trade-off, a transfer to the Pd-only catalyst was also possible. However, the characterisation results already revealed, the alloyed catalyst apparently undergoes very complex structural changes during the aging procedure and HAADF-STEM even showed the tendency of few Pt/Pd particles to segregate. Hence, an application of the above mentioned formulae is not possible.

In contemplation of describing the structure-insensitive reactions accordingly, scaling the rate constants $k_{0,i}$ with the relative loss of dispersion due to aging should suffice:

$$\text{Eq. 4} \quad k_{0,i}^{(t,T)} = \frac{D(t,T)}{D_0} \cdot k_{0,i}$$

However, it was observed, that this approach does not work on all three types of catalysts in order to account for the complex hysteresis behaviour after aging. Instead, various scaling factors F_i needed to be incorporated for several groups of reactions:

$$\text{Eq. 5} \quad k_{0,i}^{(t,T)} = F_i \cdot k_{0,i}$$

Using this strategy, the number of parameters that need to be calibrated to describe the aged catalyst can be significantly reduced. A detailed description of the procedure can be founded in [3]. **FIGURE 3** shows experimental data and simulation results of an aged catalyst (700 °C, 16 h) when NO, CO, and propene are present in the feed.

6 SUMMARY

Based on extensive measurements on a synthetic-gas isothermal test-bench a phenomenologically motivated, global kinetic model for all three types of Pt-, Pd- and Pt/Pd-catalysts has been developed, which accounts for the observed hysteresis phenomena in the conversion branches. In particular, the mutual influence of the noxious substances CO, NO, and propene can be described. The

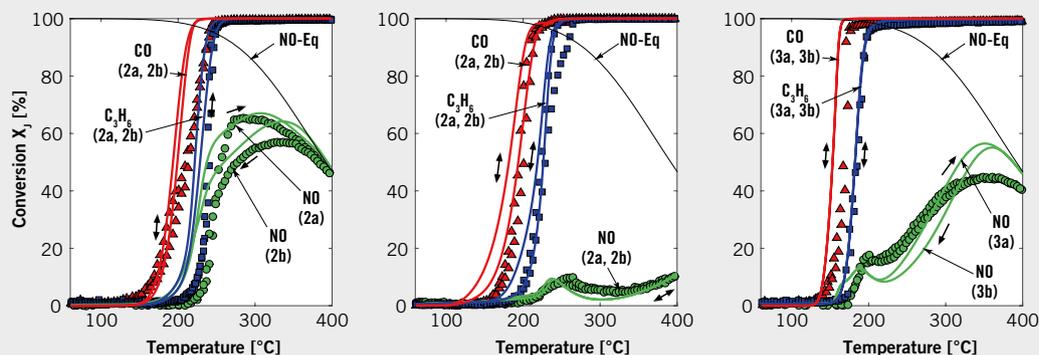


FIGURE 3 Experimental and simulation results with feed 800 ppm CO, 500 ppm NO, and 300 ppm C₃H₆ (on Pt-only (left), Pd-only (centre) and Pt/Pd (right) for the aged catalyst (700 °C, 16 h); again only the quasi-stationary cycle is presented) © ICVT)

catalyst characterisation revealed that the alloyed Pt/Pd catalyst shows a very heterogeneous morphology in the fresh state. During aging, additionally noble metal separation can occur, which prevents the existing aging-correlation from working. For the global kinetic description of the catalyst a technique is proposed, where several factors are used to scale the reaction rate constants, minimising the effort of reparametrisation. Hereby, an appropriate prediction of the conversion behaviour is possible.

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THANKS

The authors want to thank the Forschungsvereinigung Verbrennungskraftmaschinen e. V. for the financial support of project No. 1141 "Platin-/Palladium-Katalysatoren: Einfluss der Zusammensetzung, der Alterung und der Edelmetalloxid-Bildung auf charakteristische Eigenschaften und reaktionskinetische Modellparameter" as well as the coordination team under the direction of Dr. Volker Schmeißer, Daimler AG. The provision of the catalysts through Dr. Martin Votsmeier, Umicore AG & Co. KG, is gratefully acknowledged.



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