

Modeling of conversion hysteresis phenomena on Pt/Pd-based Diesel Oxidation Catalysts

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Highlights

- Diesel oxidation catalysts are reversibly deactivated by oxide formation
- Oxide formation causes strong conversion hysteresis
- Hysteresis phenomena are strongly affected by feed composition
- A kinetic model was developed to represent conversion hysteresis

1. Introduction

Diesel Oxidation Catalysts (DOC) play a key role in diesel exhaust aftertreatment systems. Typical noble metals used as active components are platinum (Pt) and palladium (Pd), or a combination of both (alloyed or multi-layered). Several publications have revealed an apparent inverse hysteresis in the NO conversion on Pt-based catalyst. This is attributed to noble metal oxidation at high temperatures and reduction by NO at low temperatures. The presence of CO and propene strongly affect the observed hysteresis phenomena. By considering the oxidation state of the catalyst together with classic Langmuir Hishelwood (LHHW) kinetics a global kinetic model is developed that is able to reproduce experimental findings in a wide range of compositions and temperatures. The model is applicable for fresh and aged catalysts.

2. Methods

Experimental:

A selection of several Pt- and Pd-only as well as PtPd alloyed monolith catalysts (Pt:Pd = 2:1) has been provided by Umicore AG & Co. KG. Slices of one channel height were prepared from the respective monoliths and tested in a metallic isothermal flat-bed reactor. The reactor was fed with synthetic exhaust gas (7% CO₂, 5% H₂O and 5% O₂ in N₂) with different amounts of noxious compounds NO, CO, and C₃H₆ (as HC representative). After a reducing pre-treatment (350 °C, 1h, 3% H₂ in N₂) several successive light-off/light-out temperature cycles with different feed composition were performed until cyclic stationary state was reached. This allowed determining the conversion behaviour of individual compounds as well as their interplay in different mixtures for the catalyst samples in a temperature range between 60 and 400°C. The procedure was applied to fresh and aged catalysts.

Global kinetic modeling:

By considering the oxidation state of the catalyst Hauff et al. were able to derive a global kinetic model for NO-conversion hysteresis on Pt-only catalysts [1, 2]. This concept was extended for the hysteresis phenomena observed in the conversion branches of NO, CO, and propene. Conventional LHHW expressions were derived for the oxidized and reduced state of the catalyst. The total reaction rate is then calculated from weighted interpolation of the reaction rates by the current oxidation state of the catalyst. In addition, rate expressions for the change of the oxidation state of the catalyst as a function of composition and temperature are developed and carefully parameterised. Parameters of reaction rates are derived sequentially for single components and mixtures thereof. The model was applied to both monometallic (Pt- and Pd-only) and PtPd alloyed monolith catalyst. Once the kinetic model has been set up for a fresh catalyst only minor reparameterization is necessary for aged catalysts.

3. Results and discussion

The model performance is evaluated for all three different kinds of catalysts. Very good agreement between

experiments and simulations is achieved for the monometallic catalysts. Exemplary results for Pt-only are presented in Fig. 1.

Here, the cyclic stationary state is presented for NO-only (*left*), NO + CO (*centre*), and NO + CO + C₃H₆ (*right*). The main reason for hysteresis is oxidation of the catalyst during light-off and reduction by NO at low temperatures. Also, thermal decomposition of oxide at high temperatures has to be accounted for [1]. The inverse NO-only hysteresis is enlarged in the presence of CO due to stronger noble metal oxide reduction during light-out (*centre*).

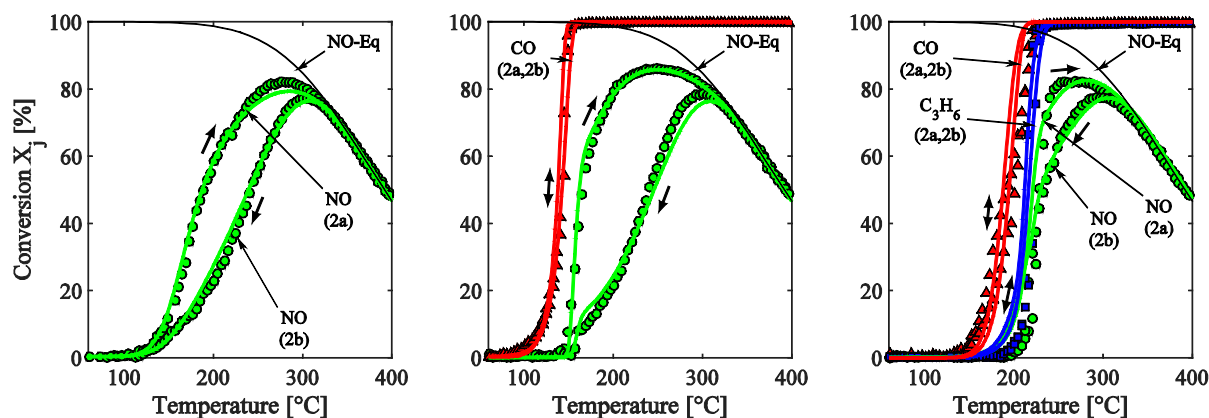


Figure 1 Experimental (symbols) and simulation results (lines) on Pt-only; *left*: NO-only (500ppm), *center*: NO + CO (500ppm / 800ppm), *right*: NO + CO + C₃H₆ (500ppm / 800ppm / 300ppm); the quasi stationary cycle is presented.

Surprisingly the well-known CO hysteresis during light-off/light-out is not observed in the presence of NO. When propene is added to the feed, the hysteresis is somewhat weaker pronounced due to mutual inhibition of the noxious gases which leads to a shift of the light-off curves to higher temperatures. A comparison with simulation results shows that the model is very well capable of reproducing the experimental findings.

Although a superposition of the models of the Pt- and Pd-only catalysts did not suffice to account for the complex behaviour of the PtPd-catalyst directly, it was nevertheless possible to apply the model *structure* to the cyclic stationary conversion, which led to acceptable results besides few deviations in NO conversion at temperatures between 250 and 350 °C.

4. Conclusions

Based on a considerably large set of experimental data, a global kinetic model for different types of diesel oxidation catalysts was developed and tested. By considering the oxidation state of the catalyst state by an additional balance equation, the causative de- and reactivation phenomena are represented with high accuracy on a Pt- and Pd-only catalysts and with some trade-off also for a Pt/Pd alloyed catalyst. The model is able to reproduce the complex hysteresis phenomena observed in the conversion branches of NO, CO, and C₃H₆.

References

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Keywords

Global kinetic model; hysteresis phenomena; diesel oxidation catalyst; reversible catalyst deactivation