

# Dynamic changes of NH<sub>3</sub> oxidation activity over Pt/Al<sub>2</sub>O<sub>3</sub>: an experimental and modelling study for automotive applications

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## Highlights

- Isothermal transient loss of activity of Pt/Al<sub>2</sub>O<sub>3</sub> towards NH<sub>3</sub> oxidation, caused by O<sub>2</sub>.
- NH<sub>3</sub> conversion hysteresis during light-off experiments
- Kinetic model including Pt oxide formation

## 1. Introduction

To decrease tail-pipe emissions of NH<sub>3</sub>, the implementation of the Ammonia Slip Catalyst (ASC) in the vehicles after-treatment systems has become of primary relevance. In the ASC, the abatement of NH<sub>3</sub> is achieved via direct oxidation over a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Although extensive research on the reaction mechanisms has been carried out [1,2], some significant open questions remain. In particular, the activity of the Pt catalyst at low temperatures (< 300 °C) has been proven to depend on the catalyst history, causing dynamic changes in activity, often observable as conversion hysteresis in light-off experiments [2]. In these experiments, for a given feed composition, a higher NH<sub>3</sub> conversion is observed if the light-off is measured during a cooling ramp, rather than a heating ramp. To the author's knowledge, a detailed mechanistic explanation for this phenomenon is still to be provided. In this study, we propose an interpretation of such phenomenon, ascribing it to a detrimental effect of oxygen, which progressively deactivates the Pt surface by Pt oxides formation. To reach this goal, transient experiments on NH<sub>3</sub> oxidation have been carried out, together with modelling of the catalyst activity.

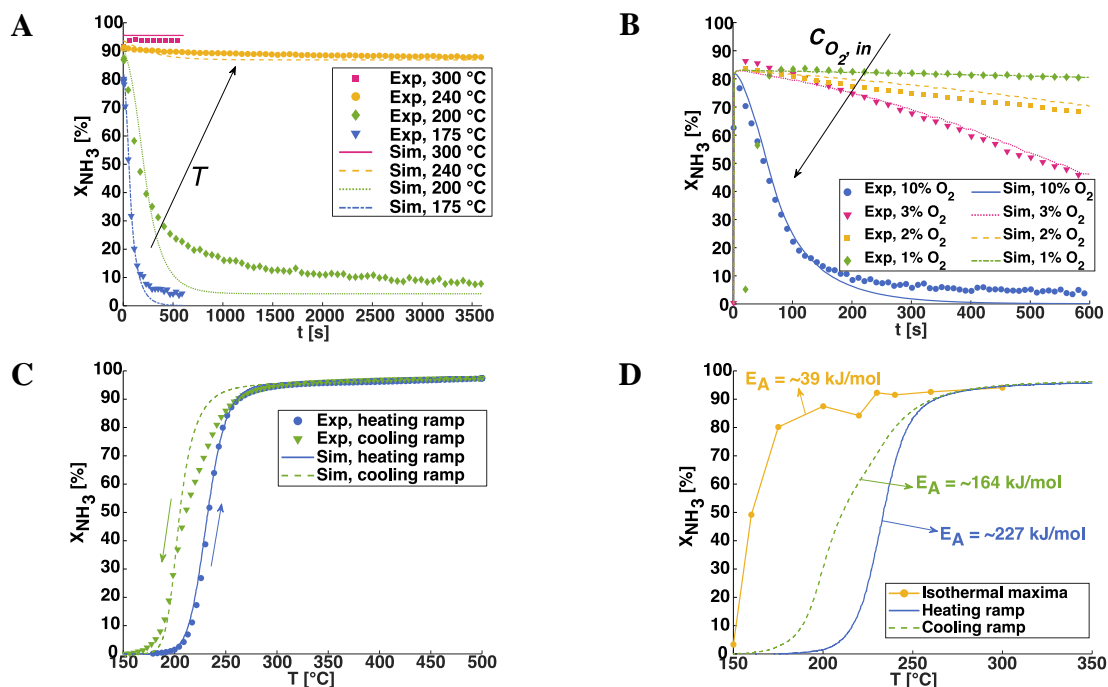
## 2. Methods

The NH<sub>3</sub> oxidation activity of an aged Pt/Al<sub>2</sub>O<sub>3</sub> wash-coated monolith has been tested at different temperatures below 300 °C and at different O<sub>2</sub> contents, using a synthetic gas test bench and an FTIR gas analyzer. Both isothermal experiments as well as light-off experiments with different temperature ramps have been used for this study. As a support to the results, a 1D+1D monolith model which included the formation of Pt oxide has been used to fit the NH<sub>3</sub> conversion profile.

## 3. Results and discussion

Figure 1A shows the NH<sub>3</sub> conversion against time during the isothermal experiments with a constant feed composition, for different fixed temperatures. At the beginning of each test, no O<sub>2</sub> is fed in the system, and no oxide is present on the Pt surface. Then, O<sub>2</sub> is fed to the reactor, initiating the NH<sub>3</sub> oxidation. An initial high conversion is reached, which has been ascribed to the conversion over an oxide-free Pt surface. Above 240 °C, this initial activity remains constant over time. Instead, at lower temperatures, the catalyst shows a slow and progressive deactivation, until a steady conversion is achieved. As shown in Figure 1B, varying the O<sub>2</sub> content directly impacts the severity of this deactivation, the faster the higher O<sub>2</sub> concentration, suggesting that this effect can be ascribed to the formation of detrimental Pt oxides over time, hindering the NH<sub>3</sub> conversion. We then have applied this concept to a 1D+1D monolith model and fitted it on the isothermal data. As shown in Figure 1A-B, a good agreement with the data is obtained. Then, the model has been used to simulate a heating-cooling light-off sequence and compared to the experimental NH<sub>3</sub> conversions (Figure 1C). The model clearly confirms the connection between the conversion hysteresis and the Pt oxides formation. Starting from a clear surface, during the cooling ramp the catalyst accumulates oxides more slowly than the temperature change, thus resulting in a mild deactivation. In contrast, the catalyst surface in the heating ramp starts with a high level of Pt oxide, which is then removed with temperature more slowly than the temperature change, resulting in a stronger deactivation. The different degree of deactivation leads to the observed hysteresis. Finally, by tuning the kinetics of our model on the isothermal conversions, we have been

able to calculate the activation energy of the oxide-free  $\text{NH}_3$  oxidation to be closer to the theoretically computed values from DFT studies [3], considerably lower than the values typically found from light-off curves, as shown in Figure 1D. Thanks to the inclusion of the detrimental Pt-oxide formation, the model is still able to capture the light-off curves, showing that the increase in the apparent activation energy in the light-off is caused by the presence of Pt oxides.



**Figure 1.** (A) Experimental and simulated transient trends of  $\text{NH}_3$  conversion from the injection of  $\text{O}_2$  in the feed, at different temperatures. (B) Experimental and simulated transient trends of  $\text{NH}_3$  conversion at different  $\text{O}_2$  contents. (C) Experimental and simulated  $\text{NH}_3$  conversion hysteresis between a heating and a cooling ramp during a light-off experiment. (D) Activation energies computed from maximum conversions in the isothermal tests (yellow), during a light-off with a heating ramp (blue) and a light-off with a cooling ramp (green).

#### 4. Conclusions

By combining experiments and kinetic modelling of  $\text{NH}_3$  oxidation over  $\text{Pt}/\text{Al}_2\text{O}_3$ , we show that isothermal dynamic changes in  $\text{NH}_3$  oxidation activity and the  $\text{NH}_3$  conversion hysteresis observed below 300 °C in conventional light-off experiments could be caused by the same effect, that is the slow formation of detrimental Pt oxides at low temperatures, as supported by the good agreement between the data and our 1D+1D model, where  $\text{NH}_3$  oxidation and detrimental Pt oxide formation have been treated as separate reactions. The formation of Pt oxides is favoured by low temperatures, and it is considerably slow, and so is their removal with increasing temperature.

As a whole, this work combines experimentally-derived intrinsic  $\text{NH}_3$  oxidation kinetics with the deactivation caused by Pt oxide formation, improving the understanding and the modelling of Pt catalyst under dynamic conditions.

#### References

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#### Keywords

$\text{NH}_3$  oxidation, Automotive Catalysis, Exhaust Control, Kinetic Model.  $\text{Pt}/\text{Al}_2\text{O}_3$ .