Deactivation of exhaust aftertreatment catalysts for heavy-duty vehicles – influence of sulfur on the activity and selectivity of Cu-SSZ-13 SCR catalysts

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Abstract: *A challenge for Cu-zeolite SCR catalysts is deactivation by impurities from fuel and engine oil, e.g. sulfur. This study investigates the effect of sulfur on the performance of Cu-SSZ-13 SCR catalysts. Lab-aged catalysts are compared with engine-aged catalysts. The study provides relevant information regarding catalyst performance and durability. This will contribute to the understanding of short and long-term catalyst degradation and an ability to produce more durable aftertreatment systems.*

Keywords: NH_3-SCR, Cu-CHA, sulfur

1. Introduction

The negative impact of diesel exhaust on environment and health has led to increasingly stringent exhaust gas regulations over the years[1]. In the future, even stricter limits are to be expected. For example, CARB (Californa Air Resources Board) proposes a considerable decrease of the NO_x limit to as low as 0.02-0.1 g/bhp-h (CARB 23)[2]. A greenhouse gas limit is very probable to be introduced as well. This puts hard demands on exhaust gas aftertreatment systems, which need to be highly efficient and durable for the vehicle to comply with the emission legislations, today and in the future. Deactivation of Cu-zeolite SCR catalyst by for example sulfur from the fuel and/or engine oil is a challenge. In the present study, the effect of sulfur on the performance of Cu-SSZ-13 SCR catalysts is investigated. The effect of sulfur exposure temperature, and the influence of the NO_2/NO_x ratio, are considered. Two different regeneration temperatures are compared. In addition, catalyst samples from an engine-aged catalyst are evaluated. The results presented in this study will lead to an increased understanding of deactivation of SCR catalysts, and provide knowledge for producing more durable aftertreatment systems.

2. Experimental

Figure 1 shows a schematic of the main part of the experimental procedure. The NH_3-SCR activity of a fresh catalyst core was tested in a laboratory reactor, thereafter the catalyst was aged – exposed to SO_2 - in the same reactor, and the activity of the sulfur-exposed catalyst was tested. Subsequently, the catalyst was regenerated and thereafter the activity was tested once more. Using this procedure, the performance of the fresh, sulfur-exposed and regenerated catalyst was measured. The procedure was repeated for four different SO_2 exposure temperatures. The performance of an engine-aged catalyst was also tested. Furthermore, elemental analysis of fresh and SO_2 exposed, both lab- and engine aged samples, were performed. Additionally, the SO_2 oxidation activity of a fresh catalyst was evaluated.

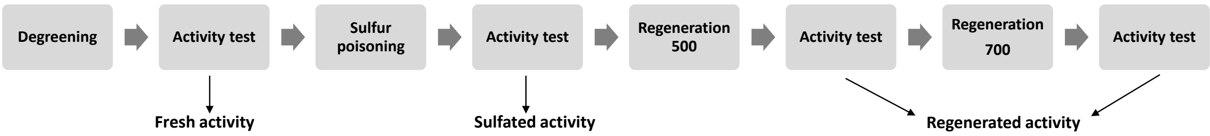

Figure 1: Experimental procedure for activity testing, sulfur exposure and regenerations. Figure adapted from Lantto´s thesis[3].

3. Results and discussion

Some of the results from the present study can be seen in Figure 2, which shows that the sulfur exposure temperature has an important influence on the degree of deactivation. Furthermore, it can be seen that the engine-aged catalyst which was evaluated is significantly deactivated. A small part of this deactivation was found to be related to sulfur.

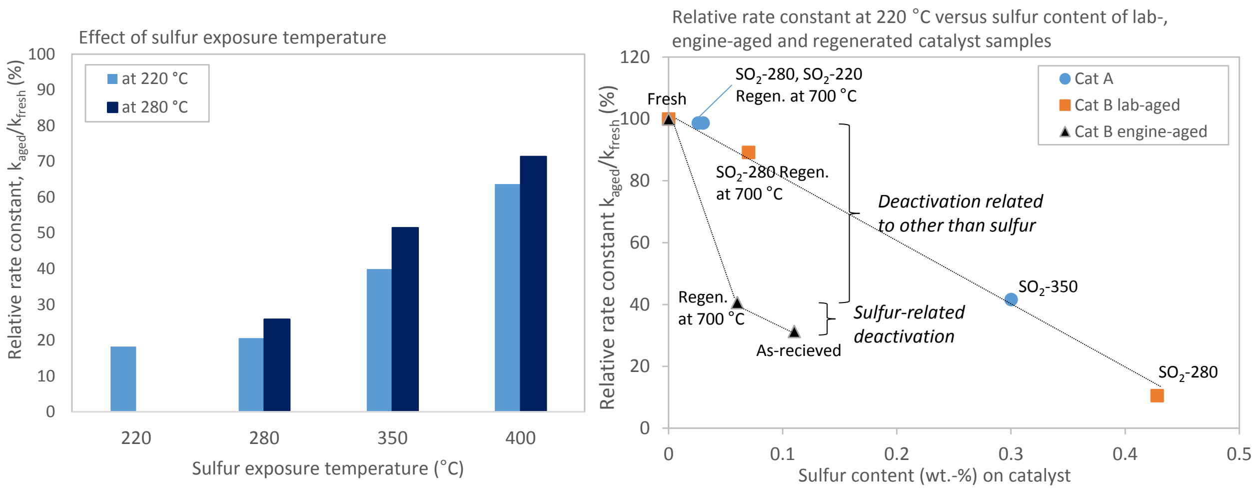

Figure 2: a) Relative rate constants at 220 and 280 °C respectively, for catalyst exposed to SO_2 at different temperatures. The sample exposed to SO_2 at 220 °C was not tested at 280 °C. b) Relative rate constant of lab- and engine-aged catalyst at 220 °C versus sulfur content of catalyst. 1000 vol.-ppm NO_x, 1000 vol.-ppm NH_3, 10 vol.-% O_2, 5 vol.-% H_2O, GHSV of 120,000 h^{-1} during the activity test.

4. Conclusions

The SO_2 exposure temperature is shown to have an important impact on the performance of the Cu-SSZ-13 catalyst at low evaluation temperatures. The lowest sulfur-exposure temperature (220 ºC) results in the most severe deactivation, while the highest temperature during sulfur exposure (400 ºC) results in the lowest degree of deactivation. This trend appears to be attributed to that more sulfur adsorbs on the catalyst at the lower sulfur exposure temperatures. A seemingly linear relationship is found between the sulfur content on the catalyst and the relative rate constant (k_{aged}/k_{fresh}) for the lab-aged catalyst samples. For the engine-aged catalyst, sulfur was responsible only for a small part of the deactivation observed.

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