

Kinetics of NH₃-oxidation and NH₃-SCR over V-based catalysts

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Introduction

NH₃-SCR is the state of art technology for NO_x abatement from power plant flue gases. The reaction ($\text{NH}_3 + \text{NO} + 1/4\text{O}_2 \rightarrow \text{N}_2 + 3/2\text{H}_2\text{O}$) involves a 1 to 1 consumption ratio, but full-scale reactors operate at NH₃/NO inlet ratios of 0.8, in order to keep NH₃ slip below 2 ppm. A strategy to enhance the NO_x abatement while maintaining NH₃ slip under this limit consists of increasing the NH₃/NO inlet ratio (*High efficiency SCR process*) in the SCR reactor and adding an extra catalyst layer able to efficiently convert the unreacted NH₃ to N₂. The same strategy is successfully applied in automotive SCR after treatment systems [1]. In order to evaluate this potential new configuration, it is necessary on one side to fully characterize the performance of the traditional SCR catalyst under the conditions of excess NH₃ concentration, where some oxidation might occur, and on the other side to identify formulations which can perform the so-called ammonia SCO downstream from the SCR layers. In this work, we address the first stage of the investigation, through a kinetic study on the reactivity of ternary V-W-Ti commercial catalysts at different V-loads. The analysis has been carried out at low NO_x inlet concentration and with alpha values ranging from 1 to 5.

Materials and Methods

Fine powders were obtained by High Dust monoliths and tested in a diluted fixed-bed microreactor. NH₃-SCR was tested with a gas mixture of 30 ppm NO, 7% H₂O, 3.5% O₂, 100 ppm SO₂, 1% CO₂ in He; NH₃/NO (α) was varied between 1.1 and 5. NH₃ oxidation was tested under the same conditions, in absence of NO, varying NH₃ concentration. Data were quantitatively analyzed by a pseudo-homogeneous 1D reactor model accounting for the possible impact of intraporous mass transfer limitations.

Results and Discussion

Fig. 1 shows in symbols the measured conversions of reactants in the NH₃-SCR tests at $\alpha = 5$, for three catalysts with low, medium and high V load. In the low temperature window, where the process was uniquely controlled by the kinetics of the SCR reaction, NO conversion increased with increasing NH₃ inlet concentration. Despite the excess of NH₃, the low concentration of reactants exalted the kinetic dependence on NH₃ surface coverage. The data collected at temperatures below 300°C were used to fit the parameters of an Eley Rideal rate expression ($r_{\text{SCR}} = k_{\text{SCR}} C_{\text{NO}} \theta_{\text{NH}_3}$), wherein ammonia adsorption was described by adopting the Temkin isotherm independently estimated by Lietti et al. [2] in a previous study.

Above 330°C, at high V load, NO conversion passed through a maximum: the overconsumption of NH₃ (also observed in [3]) along with the production of NO were herein interpreted as the evidence of unselective NH₃ oxidation to NO ($\text{NH}_3 + 5/4\text{O}_2 \rightarrow \text{NO} + 3/2\text{H}_2\text{O}$).

NH₃ oxidation was then studied by dedicated tests and Fig. 2 reported in symbols the measured conversion of NH₃ and the corresponding outlet concentration of NO. NH₃ conversion decreased with increasing inlet concentration: data were in fact well described by a simple rate expression of the form: $r_{\text{OX NH}_3} = k_{\text{OX NH}_3} \theta_{\text{NH}_3}$, which incorporated the same coverage-dependent heat of adsorption as proposed in [2]. An important result was the almost

complete selectivity to N₂: only traces of NO were detected at the reactor outlet with no formation of other NO_x species. However, by assuming an indirect reaction scheme, wherein NH₃ oxidation leads to the formation of NO which in turn prompts the SCR reaction, a good description of the results was obtained. The indirect reaction scheme is fully compatible with the apparent selectivity of the global oxidation process, due to the large difference of the intrinsic rates of NH₃-oxidation and NH₃-SCR; this is such that NO is produced up to a critical value (few ppm) at which it becomes a stationary intermediate. The complete kinetic scheme (NH₃-SCR + NH₃-oxidation) was validated by simulating the SCR tests over the entire T-range (lines in Fig. 1 at T>300°C are predictions) and a very satisfactory match was found.

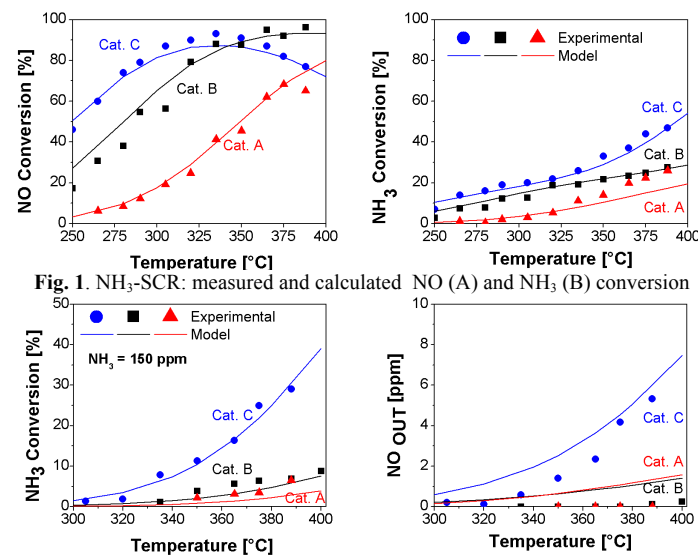


Fig. 1. NH₃-SCR: measured and calculated NO (A) and NH₃ (B) conversion

Fig. 2. NH₃-Oxidation: measured and calculated NH₃ conv. (A) and NO outlet conc. (B)

Significance - The results of this study give new perspectives to the design of *High Efficiency* SCR reactors, operating at NH₃/NO close to 1. The impact of the rate and stoichiometry of NH₃ oxidation (herein studied) within the monolith wall could be crucial on the final performance of the reactor (e.g. NO conversion and NH₃ slip); its accurate description is a prerequisite for correctly estimating the final composition of the gas stream, and thus addressing on a truthful basis the design of a possible “SCO” bed layer.

References

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