REMOVAL OF NITROGEN OXIDES FROM DIESEL EXHAUST: LABORATORY STUDIES FOR DEVELOPMENT OF AN SCR-CATALYST-SYSTEM USING SOLID UREA AS REDUCING AGENT

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Abstract

Major air pollutants emitted by DIESEL- and lean-OTTO-engines are nitrogen oxides (NO\textsubscript{x}, mostly NO), hydrocarbons (HC), carbon monoxide (CO) and soot. To eliminate NO\textsubscript{x} so far one procedure has been studied in detail: the classical selective catalytic reduction (SCR), where NO\textsubscript{x} is very selectively reduced by ammonia (NH\textsubscript{3}) to yield nitrogen and water. The German automobile industry has decided to generate on board gaseous NH\textsubscript{3} from urea ((NH\textsubscript{2})\textsubscript{2}CO). But, instead of applying an aqueous urea solution of eutectic composition, solid urea is examined in this work. Concerning the application to trucks as well as to passenger cars the following two main specifications need to be fulfilled: Increase of NO\textsubscript{x} reduction activity below 200°C and enhanced dynamics of reductant supply avoiding ammonia slip. That corresponds best with a structured catalyst arrangement (called V-H-R-O system) based on a pre-catalyst (V), an urea decomposition catalyst (H), a NO\textsubscript{x} reduction catalyst (R; conventional SCR) and an ammonia oxidation catalyst (O). A dosing apparatus with a rotating brush is applied in laboratory to proportion solid urea as fine aerosol in high reproducibility and sufficient dynamics. Below 200°C incomplete hydrolysis of urea on the H catalyst has been observed; i.e. besides desired gaseous NH\textsubscript{3}, the reactive isocyanic acid (HNCO) is formed and beyond that NH\textsubscript{3} formation follows very slowly load variations of the urea dosing system. Above 200°C online dosing of solid urea replaces gaseous NH\textsubscript{3} fairly good and this procedure has been found to be more advantageous than using aqueous urea solution of eutectic composition. For NO\textsubscript{x} reduction commercial TiO\textsubscript{2}(anatas)-based V\textsubscript{2}O\textsubscript{5}/WO\textsubscript{3} containing catalysts (R) exhibit high activity, good N\textsubscript{2} selectivity and sufficient thermal stability up to at least 650°C. Substantial increase of the NO\textsubscript{x} conversion is achieved by raising the NO\textsubscript{2}/NO\textsubscript{x} ratio in the raw exhaust; the optimum ratio was found to be 0.5. To increase the NO\textsubscript{2} amount platinum containing pre-catalyst (V) is fixed in front of the reduction catalyst according to the principle „oxidation before reduction“. Below 200°C the NO oxidation activity of the V catalyst is adversely affected in the presence of hydrocarbons and CO. Above 250°C NO\textsubscript{2}/NO\textsubscript{x} ratios higher than 0.5 lead to an undesirable increasing NH\textsubscript{3} consumption and to less N\textsubscript{2} selectivity whereas below 200°C solid ammonium nitrate storage occurs. Later on, above 200°C NH\textsubscript{3}NO\textsubscript{3} decomposes to form the unwanted N\textsubscript{2}O. The NH\textsubscript{3} slip caused by sudden load variations is considered particularly critical. This slip needs be eliminated by the oxidation catalyst (O), which forms selectively N\textsubscript{2}. During continuous NH\textsubscript{3} load substantial quantities of N\textsubscript{2}O and NO are emitted whereas an increased N\textsubscript{2} selectivity is
registered during pulse-type NH₃ load that will be recommended. Summarizing, the application of solid urea for the SCR technology is recommended.

**Keywords:** NO reduction, solid urea SCR technology, V₂O₅-WO₃/TiO₂ catalyst