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

Werner Weisweiler

Universität Karlsruhe, Institut für Chemische Technik, Kaiserstr. 12, D-76128 Karlsruhe, GERMANY

Abstract

Major air pollutants emitted by DIESEL- and lean-OTTO-engines are nitrogen oxides (NO_x , mostly NO), hydrocarbons (HC), carbon monoxide (CO) and soot. To eliminate NO_x so far one procedure has been studied in detail: the classical selective catalytic reduction (SCR), where NO_x is very selectively reduced by ammonia (NH_3) to yield nitrogen and water. The German automobile industry has decided to generate on board gaseous NH_3 from urea ($(\text{NH}_2)_2\text{CO}$). 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_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_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_3 , the reactive isocyanic acid (HNCO) is formed and beyond that NH_3 formation follows very slowly load variations of the urea dosing system. Above 200°C on-line dosing of solid urea replaces gaseous NH_3 fairly good and this procedure has been found to be more advantageous than using aqueous urea solution of eutectic composition. For NO_x reduction commercial TiO_2 (anatase)-based $\text{V}_2\text{O}_5/\text{WO}_3$ containing catalysts (R) exhibit high activity, good N_2 selectivity and sufficient thermal stability up to at least 650°C . Substantial increase of the NO_x conversion is achieved by raising the NO_2/NO_x ratio in the raw exhaust; the optimum ratio was found to be 0.5. To increase the NO_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_2/NO_x ratios higher than 0.5 lead to an undesirable increasing NH_3 consumption and to less N_2 selectivity whereas below 200°C solid ammonium nitrate storage occurs. Later on, above 200°C NH_4NO_3 decomposes to form the unwanted N_2O . The NH_3 slip caused by sudden load variations is considered particularly critical. This slip needs to be eliminated by the oxidation catalyst (O), which forms selectively N_2 . During continuous NH_3 load substantial quantities of N_2O and NO are emitted whereas an increased N_2 selectivity is

registered during pulse-type NH_3 load that will be recommended. Summarizing, the application of solid urea for the SCR technology is recommended.

Keywords: NO reduction, solid urea SCR technology, $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst
