Development of New Diesel Oxidation and NH3 Slip Catalysts

Diezel engines used in the transport sector and other heavy machinery form pollutants during the combustion process. Emission of these pollutants into the atmosphere has harmful consequences on human health and the environment. In order to mitigate these harmful effects, regulations have been imposed by environmental protection agencies on the most significant pollutants, including CO, hydrocarbons, NOx, and particulate matter. To reduce emissions to the levels specified by the recent Euro VI regulations, it is necessary to apply catalytic exhaust gas aftertreatment systems.

A modern diesel exhaust aftertreatment system commonly consists of a Pt-based diesel oxidation catalyst (DOC) to oxidize CO and unburnt hydrocarbons to CO2 and H2O, and oxidize NO to NO2. This is followed by the diesel particulate filter (DPF), which entraps particulate matter from the exhaust gas. A solution of urea is injected after the DPF to supply NH3 for the selective catalytic reduction (SCR) of NOx over an NH3-SCR catalyst. A mixture of NO and some NO2 evokes the fast SCR reaction, which increases NOx reduction. Emissions of NOx can be further decreased by dosing a stoichiometric excess of NH3. However, NH3 is also a regulated pollutant and it is therefore necessary to include an ammonia slip catalyst (ASC) for the selective catalytic oxidation of excess NH3 to N2 and H2O.

The purpose of this research project has been to develop an optimized diesel oxidation catalyst with a low noble metal content and a highly active ammonia oxidation catalyst with an improved N2 selectivity. The Pt-based DOC constitutes a significant part of system costs. To effectively utilize the platinum and reduce cost, the influence of Pt particle size on catalytic activity for CO, hydrocarbon, and NO oxidation was studied using 1 wt.% Pt/Al2O3 catalysts with Pt particles diameters between 1.3 and 18.7 nm. The mass based oxidation activity of CO, C3H6, and NO showed an optimal Pt particle size between 2–4 nm for all three reactions. Based on the turnover frequencies and the distribution of surface atoms of Pt particles, the reactions appear to be mainly catalyzed by terrace atoms, which are most abundant between 2–4 nm. The decrease in catalytic activity for large Pt particles can be explained by the diminishing Pt surface area, while the decrease in activity for small particles is due to the lack of terrace atoms required for catalyzing the oxidation of CO, hydrocarbons, and NO.

The modern ASC is a multi-functional catalyst that combines the high ammonia oxidation (AMOX) activity of a Pt-based catalyst with the capability of an SCR catalyst to reduce formed NOx to N2 using NH3. The high selectivity of the AMOX catalyst towards N2O and NOx at temperatures above 225–250°C, corresponding to a poor N2 selectivity, is counterproductive for the aftertreatment system. By including an SCR catalyst, the N2 selectivity is greatly improved. The AMOX component of the ASC was considered by investigating the catalytic oxidation of NH3 over a series of noble metal catalysts (1 wt.% Pt/Al2O3, 5 wt.% Pt/Al2O3, 5 wt.% Rh/Al2O3, and 5 wt.% Pd/Al2O3). The Pt catalysts were the most active and a series of Pt/Al2O3 catalysts with varying Pt particle sizes of 1.3–18.7 nm and of ~200 nm was subsequently tested. Large Pt particles of 7.7 nm, 18.7 nm, and ~200 nm were the most active, and Pt particles of ~200 nm also achieved lower yields of N2O and NOx, but with an increase in the total NOx formed. Furthermore, Pt particles of 2–4 nm achieved the greatest NOx/NO2 ratios, in line with observations for NO oxidation over 1 wt.% Pt/Al2O3.

A single channel 1D-1D steady state mathematical model of the ammonia slip catalyst was further developed and validated in order to improve system understanding and reduce experimental efforts. The model includes film diffusion from the gas channel to the washcoat surface, and the diffusion and reaction throughout the washcoat layers of one monolithic channel. The kinetic models applied were derived based on activity measurements for 1 wt.% Pt/TiO2-SiO2 (AMOX) and 3.5 wt.%Cu-BEA (SCR). The monolith model was validated against experimental data for NH3 oxidation over four monolithic catalysts: single layer AMOX, single layer SCR, single mixed layer, and dual layer configurations. The model description agrees well with experimental data for NH3 conversion and selectivities to NOx, N2O, and N2.

The validated model was used to analyze the performance of the single layer and dual layer ammonia slip catalysts with respect to variations in the following parameters: the intrinsic activity of the AMOX catalyst, the loadings of the AMOX and SCR catalysts, the effective diffusivity of the catalyst layers, the NO oxidation activity of the AMOX catalyst, and the ability of each catalyst to form N2O. For all ASC catalysts, an adequate Pt loading is necessary since it determines the ammonia oxidation activity available. If the Pt loading is sufficient, then the catalyst loading and effective diffusivity become the key design parameters since these factors determine the effectiveness factor of the catalyst and the magnitude of SCR activity available for NOx reduction. By varying the NO oxidation activity of the AMOX catalyst it is possible to alter the NOx/NO2 ratio and evoke the fast SCR reaction, thereby improving NOx reduction, but also increasing N2O selectivity. Addition-ally, excluding N2O formation from either the AMOX or SCR catalyst identified the AMOX catalyst as the main source of N2O formation. Thus, development of an ASC with low N2O yield should focus on the AMOX component. The multi-objective optimization of ten ASC configurations for NH3 oxidation at 300°C was used to study the sensitivity towards the catalyst architecture of the ASC. The resulting Pareto fronts indicate that the optimal catalyst systems with the most potential are those involving mixed layers of AMOX and SCR catalysts, rather than pure layers of AMOX or a top layer of SCR. This is mainly due to the ability of the mixed layers to circumvent N2O formation with the more immediate reduction of NOx with NH3.

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