Selective Ammonia Oxidation on Multi-Layer Cu-SSZ-13/Pt/Al\textsubscript{2}O\textsubscript{3} Monoliths

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**Introduction**

Selective catalytic reduction (SCR) of NO\textsubscript{x} (NO + NO\textsubscript{2}) with NH\textsubscript{3} on metal (Cu- and Fe-) exchanged zeolites is used to comply with the strict NO\textsubscript{x} emission standards [1]. NH\textsubscript{3} is produced on-board by hydrazine urea and is injected upstream of the SCR catalyst. One challenge of this technology is that unreacted NH\textsubscript{3} can escape the reactor due to desorption of the stored NH\textsubscript{3} during an exhaust temperature increase, overdosing of NH\textsubscript{3}, or SCR catalyst deactivation [2,3]. This ‘NH\textsubscript{3} Slip’ is undesired and some European countries have regulations on the amount of its emissions due to its odor. The “Ammonia Slip Catalyst” (ASC) is positioned downstream of the SCR catalyst to selectively oxidize NH\textsubscript{3} to N\textsubscript{2} in order to prevent its emission. There is a need for further development of ASC technology to minimize the formation of undesired products NO\textsubscript{x} and N\textsubscript{2}O. Furthermore, the aftertreatment technology application requires the ASC to work under very challenging conditions such as low temperature, high space velocity, and widely varying exhaust gas composition. Finally, the ASC is expected to show good hydrothermal stability. The state-of-the-art ASC uses a dual-layer architecture with Pt/Al\textsubscript{2}O\textsubscript{3} bottom layer and a Cu- or Fe-exchanged zeolite top layer [4,5]. This architecture is used to decrease the selectivity to undesired products by reducing the undesired intermediate NO\textsubscript{x} formed on Pt/Al\textsubscript{2}O\textsubscript{3} over SCR catalyst. Therefore, the SCR component plays an important role in controlling the selectivity to undesired products.

In this contribution the investigations of the impact of catalyst formulation as well as diffusion parameters, achieved by varying the SCR washcoat thickness, on the NH\textsubscript{3} conversion and selectivity to different products over Cu-SSZ-13/Pt/Al\textsubscript{2}O\textsubscript{3} coated monoliths will be presented.

**Materials and methods**

A 0.15wt% Pt/Al\textsubscript{2}O\textsubscript{3} catalyst was synthesized by an incipient wetness impregnation method using H\textsubscript{3}PtCl\textsubscript{6}, H\textsubscript{2}O (Sigma Aldrich, USA). The Na-SSZ-13 synthesized by Chalmers was ion exchanged with NH\textsubscript{4}NO\textsubscript{3} followed by Cu(NO\textsubscript{3})\textsubscript{2} to obtain Cu-SSZ-13. XRD was used to examine that correct structure was received and elemental analysis of the powder was conducted with ICP-SFMS, resulting in a Si/Al ratio of 3.63 and a copper loading of 3.1wt\%.

The 0.8 cm diameter cordierite substrates of 400 cells per square inch, were washedcoated with the slurries containing the above catalysts in order to obtain i) Cu-SSZ-13/Pt/Al\textsubscript{2}O\textsubscript{3}, dual layer structure with bottom layer being oxidation catalyst and the top layer SCR catalyst, ii) single layer containing mixture of Cu-SSZ-13/Pt/Al\textsubscript{2}O\textsubscript{3}, iii) Pt/Al\textsubscript{2}O\textsubscript{3} and iv) Cu-SSZ-13. When used the SCR catalyst loading on the monolith was between 1 to 3 g/in\textsuperscript{3} while the oxidation catalyst loading was fixed at 1.4 g/in\textsuperscript{3}.

A bench top reactor, described elsewhere [4], was used for evaluating the reactivity of the catalysts. The total flow rate was maintained at 1000 sccm, corresponding to a GHSV of 66k h\textsuperscript{-1} for 2 cm long monolith and 265k h\textsuperscript{-1} for 0.5 cm long monolith. The feed concentration of 500 ppm NH\textsubscript{3} was used with varying levels of NO (0 – 500 ppm) along with 5% O\textsubscript{2}, 2.5% H\textsubscript{2}O, 2% CO\textsubscript{2} and balance Ar. An FT-IR was used to measure NO, NO\textsubscript{2}, N\textsubscript{2}O, NH\textsubscript{3}, CO\textsubscript{2} and H\textsubscript{2}O species concentrations. The gas lines were heated to above 150°C to avoid adsorption and condensation of H\textsubscript{2}O and NH\textsubscript{3}.

**Results and discussions**

The impact of the SCR catalyst loading, varied between 0 and 3g/in\textsuperscript{3}, on the NH\textsubscript{3} oxidation activity of dual layer Cu-SSZ-13/Pt/Al\textsubscript{2}O\textsubscript{3} ASCs are shown in Figure 1(a). The NH\textsubscript{3} conversion decreased due to the presence of SCR catalyst layer and with the increase in SCR catalyst layer thickness, which was clear between 250 and 350°C. Below 350°C the SCR catalyst contribution to direct NH\textsubscript{3} oxidation by oxygen is minimal and thus the observed decrease in activity is attributed to a lower mass transfer of NH\textsubscript{3} through the SCR layer which acts as a barrier. On the other hand, the presence of the CuSSZ-13 top layer dramatically increased the N\textsubscript{2} yield compared to a discrete Pt/Al\textsubscript{2}O\textsubscript{3} catalyst and above 350°C with the selectivity to N\textsubscript{2} increasing sharply with increase in SCR catalyst loading.

In the presentation the observed differences in NH\textsubscript{3} conversion and N\textsubscript{2} yield will be explained based on i) increased resistance to NH\textsubscript{3} mass transfer to bottom layer Pt/Al\textsubscript{2}O\textsubscript{3}, ii) conversion of NO\textsubscript{x}, produced in Pt/Al\textsubscript{2}O\textsubscript{3} bottom layer, through reaction with NH\textsubscript{3} in the top layer SCR catalyst, iii) direct and selective oxidation of NH\textsubscript{3} above 350°C in the SCR catalyst which increases with an increase in SCR catalyst loading, and iv) species distribution leading to various redox reactions with different rates along the axial direction.

**Significance**

This work demonstrates the application of engineering principles to design catalyst with tunable activity and selectivity properties and to further the advancement of NH\textsubscript{3} slip catalyst technology to mitigate the diesel engine emissions.

**References**