

Title: Low Temperature Catalysts for the Selective Catalytic Reduction of Nitric Oxide

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Introduction:

Highly active low temperature catalysts for the Selective Catalytic Reduction (SCR) of nitric oxide from stationary emission sources have been developed. The catalysts exhibit NO_x reduction efficiencies of 90% or higher in the temperature range of 120°C to 300°C, at a space velocity of 10,000 h⁻¹. The effects of changes in the concentrations of water vapor, oxygen and SO₂ were studied. While increase in water vapor and oxygen concentrations increased the NO conversion, increase in SO₂ concentration decreased the NO conversion.

Experimental:

A typical flue gas composition of 400 ppm NO, 400 ppm NH₃, 5% O₂, 13% CO₂ and 8% water vapor was employed for the testing of these catalysts. The experiments were conducted in a tubular fixed bed quartz reactor with an I.D. of 13mm. Nitric oxide was analyzed using a chemiluminescence detector. Quantification of ammonia was performed by absorption of ammonia in a dilute solution of phosphorus acid for a known amount of time and then measuring the ammonium ions in the solution using an ammonia selective electrode. The catalysts tested were either in the form of 1/16th inch extrudates or 250-300 micron diameter particles.

Results and Discussion:

The nitric oxide conversion levels of the catalysts reduced by 5-10% after the addition of water vapor, compared to the NO conversions observed under dry flue gas conditions. Six catalysts were found to possess high activities for NO reduction during the initial screening of catalysts. Those catalysts exhibited conversion levels $\geq 95\%$ at different temperatures in the range of 100°C to 300°C. The most active catalyst achieved a nitric oxide reduction efficiency of 99% at 120°C.

Initial experiments with SO₂ on the best catalyst were carried out at 160°C and with a SO₂ concentration of 55 ppm. The conversion of the catalyst reduced from 99% to 24% with the addition of SO₂, but with progress of time the conversion increased to 47%. However, as soon as SO₂ was removed from the feed stream, the conversion increased back to 99%. This indicates that the effect of SO₂ on the catalyst was reversible.

The effect of changes in the water vapor concentration on the catalyst conversion in the presence of SO₂ was investigated. A 50% increase in the NO conversion was observed when the moisture content was

increased from 8% to 20%. A further increase in the water vapor concentration to 32% showed a very small increase in the NO conversion.

It is possible that SO_2 is being oxidized to SO_3 on the catalyst surface. The water vapor present in the stream would then react with the adsorbed SO_3 to form sulfuric acid which would then leave the reactor in the effluent stream. Once the adsorbed SO_3 had reacted with water vapor, that particular adsorption site would be ready to adsorb SO_2 , SO_3 or NO again. At a particular concentration of water vapor in the feed stream, the adsorption and subsequent reaction of SO_3 with water vapor should come to a steady state, indicated by a steady state conversion of NO. However, an increase in the concentration of water vapor in the feed stream would result in a shift in the equilibrium towards the formation of sulfuric acid. This in turn would remove a higher amount of SO_3 from the active sites and making these sites available for NO adsorption. This would explain the increase in the NO conversion with an increase in the concentration of water vapor in the feed stream.

Based on the above hypothesis, an increase in the concentration of oxygen in the feed stream would further facilitate the oxidation of SO_2 to form higher amounts of SO_3 , which would subsequently react with moisture to form sulfuric acid, thereby vacating the adsorption site. Therefore an increase in the oxygen concentration would again increase the NO conversion based on the same reasoning. An increase in oxygen concentration from 5% to 20% does increase the NO conversion by about 30%, thereby adding validity to the hypothesized reaction mechanism.

The effect of SO_2 on the nitric oxide reduction efficiency was also studied. Steady state NO conversions of 82%, 43%, and 22% were observed for feed SO_2 concentrations of 55 ppm, 112 ppm, and 395 ppm respectively, with 20% moisture and 20% oxygen in the feed stream.

Conclusions:

Highly active catalysts for the reduction of nitric oxide using ammonia at low temperatures have been developed. On exposure to SO_2 reversible deactivation of the catalyst is observed. In the presence of SO_2 , increases in water vapor and oxygen concentrations improve the conversion of NO. The nitric oxide conversion levels decrease with increase in SO_2 concentration.