

CATALYSTS FOR DIRECT DECOMPOSITION OF NO_x IN EXHAUSTS

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Eltron Research, Inc. is pursuing the rational development of catalysts for direct (reagentless) decomposition of NO_x. This is the most economical imaginable approach for post-combustion removal of nitrogen oxides since costs for reagent and reagent delivery (i.e., ducting, etc.) are eliminated and catalysts demonstrating activity to the present time are inexpensive (\$1 - \$4/lb).

Eltron is developing two distinct classes of catalysts for use in two distinct temperature ranges. The “low temperature” catalysts are being investigated for utility boiler applications, for which require a catalyst temperature of less than 350°C is anticipated. The “high temperature” catalysts are being developed for potential application in a number of systems including post-combustion removal of NO_x from the exhausts of gas turbines, high temperature pyrolyzers, and high temperature (e.g., glass) furnaces. The two classes of catalysts possess some crucial differences which must be understood if effectiveness is to be achieved. For example, low temperature catalysts must be designed to spillover oxygen from the active site while possessing minimal NO oxidation activity. In contrast, high temperature catalysts must possess considerable thermal, chemical, and areal stability so that surface metal-oxygen bond strengths must be greater than those in low temperature catalysts.

Performance data obtained to date may be summarized as follows. In the case of low temperature catalysts, over 40% reagentless conversion to nonoxidation products has been obtained in 3.6 % O₂ and at 4100h⁻¹ and 300°C after over 1000 hours on-line under these conditions. These catalysts have shown tolerance to as much as 18% CO₂ and 2% H₂O. However, SO₂ at greater levels than 3% of the NO concentration has been found, at low temperatures, to suppress catalyst activity. An additional feature of these catalysts is their direct N₂O decomposition activity. High temperature catalysts have exhibited NO_x conversions of 30% at 400°C and up to 32% at 1000°C. However, the latter data was obtained at space velocities between 45 and 60 thousand h⁻¹. Measurable activity has been obtained at space velocities of up to 800,000 h⁻¹. Results suggest the potential efficacy of these catalysts for the direct decomposition of nitrogen oxides in high temperature (400 - 1000°C) exhaust gases, in e.g., gas turbine and diesel engines.

The decomposition of nitrogen oxides under lean conditions absent added reductant is a particularly attractive approach for removal of NO_x from exhaust streams of diesel engines, lean burn engines, gas turbines, incinerators, and high temperature process streams. Direct decomposition catalysts have been previously reported in the literature.¹⁻⁶ Many of these results were obtained under experimental conditions of high NO concentrations(>>1000

ppm) and absent oxygen. Such conditions do not reflect the fact that a few hundred ppm of nitrogen oxides compete with oxygen concentrations of up to 15 volume percent. This three order of magnitude disadvantage renders impractical any catalyst which does not make use (through Lewis acid-base properties) of the relative acid strengths of nitrogen oxides and oxygen.

In addition to acid - base interactions between catalyst and nitrogen oxides, other phenomena must occur. For example, the role of oxygen ion vacancies and their relationship to deNO_x activity has been clearly demonstrated in the literature.^{2,3,6} The adsorbed oxygen anion resulting from dissociation is discharged via oxidation by a transition metal species in the catalyst, followed by combination into molecular oxygen and its subsequent desorption. Reoxidation of transition metal species occurs via desorption of molecular oxygen. Consideration of these requirements has led us to develop new materials based on the brownmillerite structure. The stoichiometries of these materials is such as to provide a high concentration of intrinsic oxygen ion vacancies, while at the same time providing overall material stability.

Catalysts described here have been prepared by the ceramic method and by decomposition of the constituent metal nitrates on a support. Phase purity was verified by x-ray diffraction. Surface areas of catalysts were obtained by measurement of uptake of nitrogen and application of the Brunauer-Emmett-Teller equation. Catalyst activities were measured by passing a simulated exhaust stream over weighed catalyst powder samples heated to the desired temperature with a furnace. The gas stream contained from 300 - 1100 ppm NO, with 3% O₂ in the case of low temperature catalysts and up to 16% O₂ with high temperature catalysts, with helium comprising the balance of the mixture. NO and NO₂ were analyzed by means of electrochemical sensors specific to these respective species. Reaction products (i.e. N₂ and N₂O) were analyzed by gas chromatography.

Unsupported high temperature catalysts were shown by X-ray diffractometry to possess the brownmillerite structure. Nevertheless, the brownmillerite phase appears to be active, since analogs of the material not containing the second phase have comparable or greater activity. The catalyst displayed a TPD spectrum showing a common feature of brownmillerite materials: a steeply ascending portion of the curve at temperatures above 700°C, corresponding to the loss of lattice oxygen. The catalyst also displayed a lower temperature desorption peak, corresponding to the desorption of relatively weakly bound surface oxygen species and suggesting that this catalyst can readily release surface oxygen, freeing sites for NO adsorption.

Low temperature catalysts were found to consist of mixtures of crystallographic phases.

Data obtained thus far point to the possibility and probability of a reagentless catalyst system for decomposition of nitrogen oxides in exhausts.

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