

Nanostructured perovskite-based oxidation catalysts for improved environmental emission control

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ABSTRACT

Global concerns over environmental pollution have resulted in increasingly stringent regulations to control the levels of critical air pollutants, such as, carbon monoxide (CO), nitrogen oxide species (NO_x), volatile organic compounds (VOC) and particulate matter (PM). These pollutants are removed by heterogeneous catalysis and the platinum group metals (PGM) remain the catalysts of choice but this situation is now complicated by the requirement for higher performance at lower costs while the PGM are experiencing escalating prices. A solution to this problem is the use of nanostructured perovskite-based Nanoxite™ catalysts engineered with unique structural features and high surface areas that enable higher catalytic efficiency at lower temperatures without sacrificing durability performance. In fact, Nanoxite is a “catalytic washcoat” product in that it simultaneously functions as the emission control catalyst while providing the bulk of the washcoat. As a result, both the PGM level and the amount of conventional washcoat materials are simultaneously reduced. Each powder particle possesses a hierarchical structure where larger micron sized particles hold the < 40 nanometer size perovskite grains. This desired arrangement facilitates easy powder handling and eliminates reactivity typically associated with discrete Nanograin materials. These perovskite-based catalyst formulations are applicable to both diesel engine and stationary emission control with respect to CO / VOC oxidation and the management of NO_x and PM.

Keywords: nanostructured, perovskite, Nanoxite, diesel, emission control, CO/VOC oxidation.

1 INTRODUCTION

Significant pollution reduction has been achieved over the last few decades as a result of the implementation of catalyst technology. The Manufacturers of Emission Controls Association (1) reported that automotive catalyst technology has cut pollution by more than 1.5 billion tons in the USA since the mid-1970s. While PGM continue to be the standard catalysts in emission control, both environmental and economic conditions have spurred the search for alternative materials. Over the last few years, Pt pricing jumped from US\$14/g to US\$33/g. Another

complicating factor is the steadily tightening of environmental regulations with respect to critical air contaminants suite of CO, NO_x, VOC and PM. These tougher standards require more efficient catalysts and lead to higher levels of PGM, with the resulting cost increases. As a result, there is a deep interest to both lower the level of PGM usage and implement alternative non-PGM or significantly reduced PGM catalyst formulations.

Several different approaches are being evaluated and these include the use of active nanomaterials, computer modeling to allow strategic placement of PGM particles for reduced usage rate, platinum (Pt) - palladium (Pd) combination, Pd-loaded perovskites, and improved precious metal thrifiting. Recently, researchers at Carnegie Mellon University (2) have quantified the possible impact of nanotechnology on the reduction of PGM usage to meet current and future standards. They estimated that the use of nanotechnology could reduce the annual PGM demand by 139 tons in 2030 while still meeting the environmental standards.

An attractive alternative is based on simple perovskite type material formulations. It is well established that perovskites with the general formula, $ABO_{3-\delta}$, exhibit catalytic activity with respect to oxidation reactions, with the performance linked to the nature and valence states of the A and B ions. However, despite many years of research, application of perovskite-based catalysts has been limited as a result of both non-competitive performance from un-optimized material structures and high levels of sulfur in the fuel streams.

With respect to material optimization, Nanox has made major improvements with its Nanograin Nanoxite™ oxidation catalyst formulations that exhibit superior performance over existing commercial technologies at significantly reduced PGM levels. Using its robust, patented Activated Reactive Synthesis (ARS) Technology, Nanox has established the capability to engineer these perovskite-based catalysts with features that enable higher conversion efficiencies of critical air pollutants at lower temperature.

Diesel fuel regulations are changing with the mandated decrease in the sulfur levels. In 2006, the amount of sulfur in diesel for on-road applications will drop to 15 ppm in the USA. Similar restrictions are being placed elsewhere in the world, with off-road reduction to follow. This is a dramatic

change from the earlier high levels and facilitates the use of base metal type chemistries.

This paper will review some of the advances made by Nanox for the use of perovskite-based catalysts for environmental emission control. Production technology, powder properties, wash coat capability and performance data will be highlighted to support the applicability of these lower cost catalysts, high performance products as diesel oxidation catalysts (DOC), and oxidation of CO and VOC. The work reported here covers a specific formulation based on lanthanum and cobalt, with doping of iron (Fe) and rare earths in the classical ABO₃ structure.

2 PRODUCTION TECHNOLOGY

Numerous methods have been presented to produce perovskite materials over the years and these techniques include precipitation, sol-gel, thermal processing, and decomposition processes (3). However, not all these techniques are capable of generating catalysts with the required structural features for high catalytic activity. The catalytic activity of perovskites is related to several parameters that include ionic conductivity, oxygen mobility in the lattice, reducibility, and oxygen sorption (4). In order to achieve a formulation that satisfy these conditions, Nanox has pioneered the ARS approach based on a thermo-mechanical technique that combines synthesis and activation to capture the critical features for catalysis.

ARS is a simple production process with strategic advantages that are summarized in Table 1 below. The process steps simply involve conventional raw materials mixing, synthesis, activation, drying and particle separation. Scalability and manufacturability are easily attainable with this technology.

MANUFACTURING	FEATURES
Capability	Varying grain size, activity
Flexibility	Composition control
Manufacturability	Process Control, automation
Safety	Aqueous, Large particles

Table 1: Activated Reactive Synthesis Technology Features

The engineered hierarchical structural arrangement allows free flowing, dust free operation while the handling of discrete nanograins is eliminated. The larger micron-sized particles hold the perovskite nanograins, as evident in Figure 1.

This structure imparts stability and easy handling while being compatible with wash coating technology in place today. This compatibility eliminates the need for any change in wash coating production processes. The sub-particle arrangement facilitates easy mixing with other wash coat additives typically used in these formulations. Shelf life data confirms that there is no activity degradation over time with standard powder storage protocols.

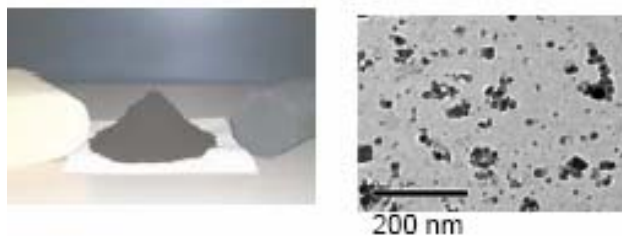


Figure 1: Hierarchical Particle & Grain Arrangement

Table 2 shows some typical properties of the basic lanthanum based formulation. Typically, the grain size exceeds 50 nm while the surface area is above 50 m²g⁻¹.

PROPERTIES	TYPICAL DATA
Chemical Composition	Lanthanum-based oxides
Structure	Crystalline
Appearance	Black Powder
Bulk Density	0.8 g cm ⁻³
Primary Grain Size	< 50 nanometres
Surface Area (BET)	> 50 m ² g ⁻¹
Mesh Size	- 200

Table 2: Typical Properties of a LaCo-based Formulation

Another advantage of the production technology is linked to the capability of producing stoichiometric materials that are free of residual raw materials and impurities that degrade activity. Figure 2 below shows a typical X-ray diffraction (XRD) profile of a lanthanum cobalt based perovskite.

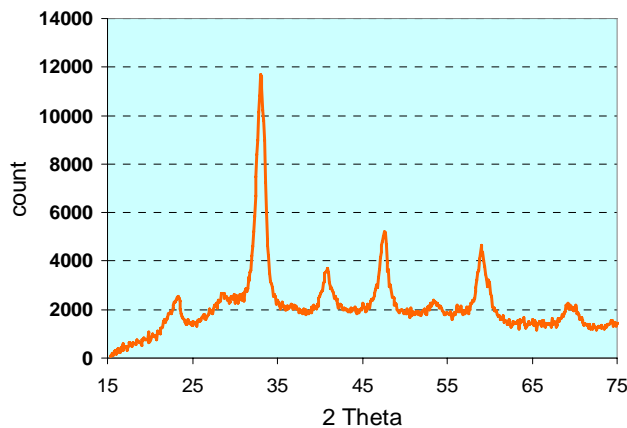


Figure 2: XRD Profile of the LaCo-based Perovskite

Perovskite formulations made with ARS have been compared with similar perovskite formulations produced by other traditional techniques. Temperature programmed desorption studies confirm a clear differentiation of the Nanoxite catalyst especially in terms of oxygen desorption and as a result, these unique features of the Nanoxite facilitate the superior catalytic performance. as shown in the comparative data summarized in Figure 3. The data is

not surprising as the Nanoxite powders exhibit better oxygen species distribution and vacancies levels that influence diffusion with the resulting higher activity.

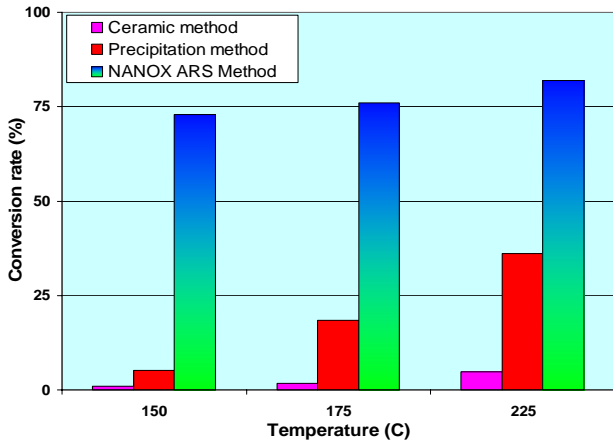


Figure 3: Catalytic Activity of Production Methods

3 WASHCOAT PREPARATION

Coating on substrates is easily completed on cordierite and metallic monoliths with aqueous 50% solids slurry, typically comprised of a mixture of 75% Nanoxite-EC1, 23% high specific surface stabilized ceria-zirconia and 2% of alumina. This solid phase is milled with water at pH 5.5 to 5.8, with loading is at 2.0 g/in³ with at least 1.5 g/in³ achievable in a single coating pass. Figure 4 shows a micrograph of the perovskite formulation coated onto a cordierite core (400 cps).

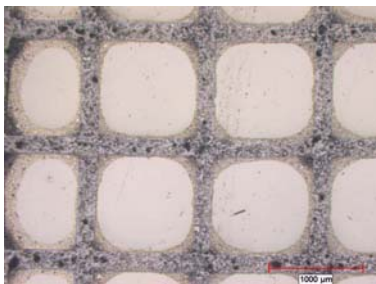


Figure 4: Cordierite Monolith with Perovskite Washcoat

4 PERFORMANCE AND APPLICATIONS

Nanoxite evaluation protocol involves the use of a gas feed stream typically composed of the following: 2000 ppm CO; 200 ppm propylene; 10% H₂O; 20% oxygen, varying levels of SO₂, and inert gas. Detection is completed by FT-IR system directly connected to the quartz micro-reactors at a GHSV of 30,000 h⁻¹. The catalysts are first “degreened” at 400 °C in the test gas stream prior to measurement of catalytic activity.

Figure 5 shows the conversion efficiencies of the Nanoxite coated onto cordierite substrate (400 cps) at a coating thickness of 2 g per cubic inch (ci), without any PGM. The data also reveal that low temperature conversion of both CO and propylene are possible in the absence of the PGM.

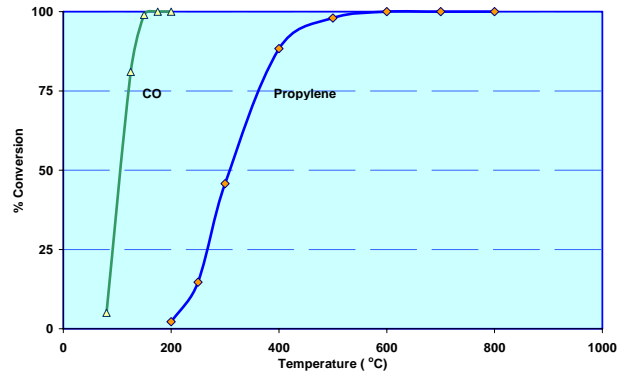


Figure 5: CO & Propylene Conversion

In durability studies, these Nanoxite catalysts maintain the high activity levels after aging for 200 hours at 450 °C in the test gas stream. The performance summarized in Figure 6 shows a stable performance profile, with the actual activity measured at 150 °C over the aging duration. The performance supports the use of these improved formulations as diesel oxidation catalysts and CO/VOC conversion.

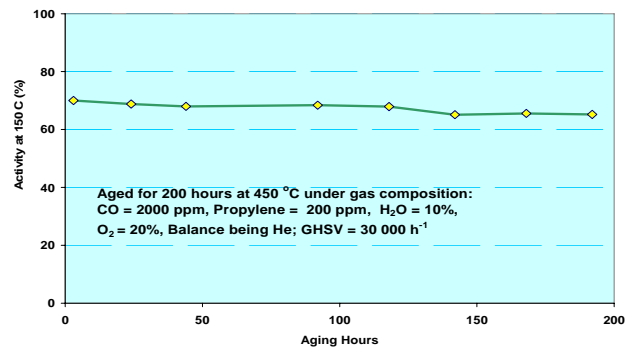


Figure 6: Hydrothermal stability of Nanoxite catalyst

Some applications may require the presence of a limited amount of Pt and/or Pd. These perovskite-based materials are quite compatible with the PGM that are easily added to the washcoat slurry to be incorporated into the perovskite-PGM type composite.

One of the challenges faced by base metal type chemistries is the presence of sulfur in the gas stream. Base metal type catalysts, as with PGM, are poisoned by sulfur dioxide. The current Nanoxite formulation has shown resistance to levels of < 15 ppm SO₂ which can translate to around 600 ppm S in the diesel fuel, assuming a 40:1 air:

feed ratio. We have also shown that addition of low levels of Pt enhances the stability with respect to sulfur poisoning.

The perovskite-based catalyst has a bi-functional role in that while it provides the catalytic conversion power, it also occupies the bulk of the washcoat layer, hence the term “catalytic washcoat”. As such, the activity is proportional to the thickness of the perovskite catalytic washcoat layer. This allows the “tuning” of activity profile through thickness control and the incorporation of smaller amounts of PGM, if needed.

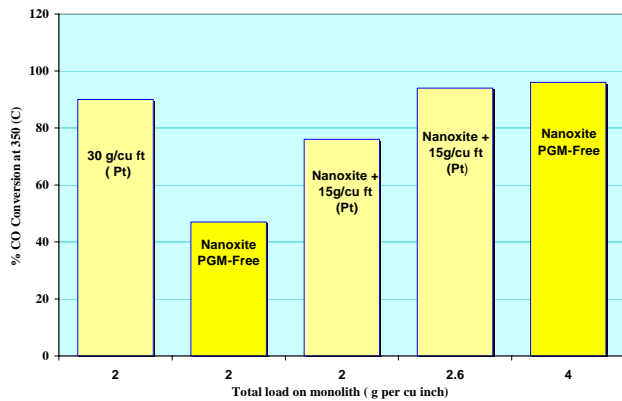


Figure 7: Effect of Nanoxite catalyst loading

Figure 7 shows the effects of this washcoat thickness variation and also the compatibility of perovskite-PGM combination with respect to the conversion of carbon monoxide. These results were obtained at a much higher space velocity of $120,000 \text{ h}^{-1}$, and with a washcoat composition of 75% Nanoxite with 25% alumina, further strengthening the value proposition of these lower cost catalysts. The data shows that a high Nanoxite coating thickness of 4 g/ci yielded a conversion efficiency higher than that obtained for a Pt catalyst loading of 30 g per cubic foot (cf). In addition, Nanoxite loading at 2.8 g/ci with Pt at 15 g/cf also showed better performance than the high Pt level of 30 g/cf. Significant cost reduction is expected through the decrease in the Pt usage.

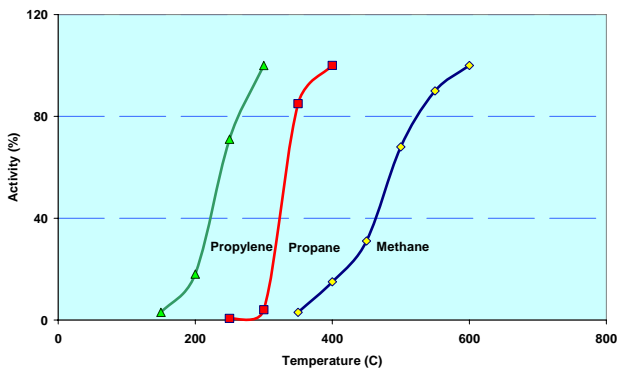


Figure 8: Catalytic Conversion of Hydrocarbons

Perovskite-based catalysts have also shown good conversion with respect to saturated hydrocarbons, such as, methane and propane. Figure 8 shows the profile of both saturated and unsaturated hydrocarbons, with the conversion efficiency higher for propylene as compared to methane. It is to be noted that this competitive conversion levels have been achieved in the absence of PGM.

5 CONCLUSIONS

The evaluation data presented in this paper provides clear and compelling incentives for the introduction of these perovskite-based catalysts in environmental emission control. Conversion of CO and VOC species are easily attained in the absence of the platinum group metals. In particular, the Nanoxite catalysts exhibited performance suitable for use as diesel oxidation catalysts (DOC) and CO/VOC oxidation.

The catalysts are manufactured from standard, conventional raw materials via robust, capable manufacturing process. The particles are strategically engineered with a hierarchical structure that confers stability while being compatible with existing industrial wash coating practices and demonstrating higher catalytic activity.

Perovskite-based catalysts are not new. These materials have been researched for decades but failed to make any significant penetration into the emission control catalyst markets. The major reasons for this situation can be simply linked to a few factors, namely, the un-optimized structures, hydrothermal stability and high levels of sulfur in the gas streams. Nanox has now changed this status with the development of its Nanoxite line of nanocrystalline perovskite-based catalyst formulations.

With the tightening of environmental emission regulation, escalating Pt pricing and demand for higher performance at lower costs, the timing for the broad use of these lower cost catalysts is now. Continuing developments are in progress to expand the applications of these materials to improved NOx management and PM reduction.

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