



High Performance, Cost-Effective Emissions Control Catalysis

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QSI has developed a comprehensive strategy based on nanoscale promoters that can be easily applied to emission control thermocatalysis. Advantages over the current commercial processes include greater control of promoter particle size, reduction in use of expensive precious metals by substitution with base metals, enhanced reaction efficiency, and improved ageing characteristics. This strategy will allow manufacturers of emissions control systems to reduce processing costs and meet new Federal and State pollution control mandates.

INTRODUCTION

Emissions regulations implemented by the EPA (Environmental Protection Agency) as initiated by the Clean Air Act of 1970 have induced OEM's (auto, system, and engine manufacturers) to improve overall engine technology state of the art. Despite extensive development, improvement in engine controls alone did not curtail exhaust emissions to mandated levels. Thus, a catalytic approach to converting noxious chemical species from engine exhausts was conceived - the development of catalysts that oxidize hydrocarbons and CO to CO₂, and reduce NO_x species (NO and NO₂) to nitrogen gas.

As a result of these developments in catalysis, a large market for emissions controls was born. The result was the development of new emission controls, with a corresponding wide network of suppliers that extends from base metal suppliers (e.g., SASOL, Rhodia, WR. Grace) to catalyst suppliers (e.g., BASF, JMI, Umicore) hardware suppliers, and system integrators (e.g., Tenneco, Eberspacher, Faurecia).

Over the last several decades, regulators have continued to tighten standards on pollutants (CO, NO_x, Hydrocarbons) and widen the range of targeted applications (off-road, construction, ATV, etc.).

The California Air Resources Board (CARB), led the way with respect to lowest emissions

requirements and timely implementation, followed closely by the EPA. The Clean Air Act allowed for individual states to have emission regulations that are tighter than federally mandated, and thus in the last five years over 16 states have opted to adopt the California emission regulations, leading to an even greater demand for emission controls and thus catalysts.

Traditionally, allowed emission levels for diesel vehicles were usually higher than for the corresponding gasoline vehicles. In general, PM (particulate matter) was not a targeted emission, especially for the heavy duty and non-road segments. This has changed with the implementation of the Tier 2 standards (2004) for light duty vehicles (LEV II for California), the 2010 Highway Rule (2010 100% of the fleet's compliance) for Class 5-8 on-road vehicles and the off-road Tier 4 regulations (2013 - 2015). High quantities of ground level ozone are still a major problem in the U.S. and the number one targeted pollutant responsible for this is NO_x emitted from diesel engines. The U.S. emission standards therefore have the lowest targeted NO_x levels compared to other parts of the world (**Fig. 1**).

Thus, there is a great need for catalysts that ensure the ever more stringent emission regulations are met and that the durability of these catalysts also allows for the longer useful life of these catalysts to be achieved. Currently emission controls for Class 8 trucks need to meet 435,000 miles useful life expectancy, while

stationary emission controls are warranted for 3 years and longer periods. In addition, all of these catalysts make use of precious metals (Platinum, Palladium, Rhodium) in various combinations and quantities, making the controls very expensive.

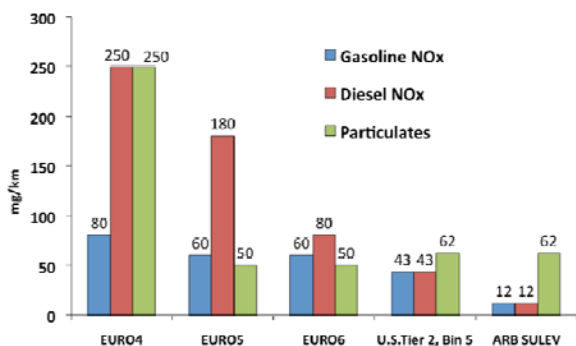


Figure 1. Comparison Between U.S. Regulations and European Standards for Both Light and Heavy Duty Vehicles, with Particular Emphasis on PM and NOx Levels.

COMMERCIAL CATALYST STRATEGY

Emission control catalysts primarily consist of precious metal nano-particles that are synthesized on the surface of support powders via metal salt solutions, such as chloroplatinic acid.

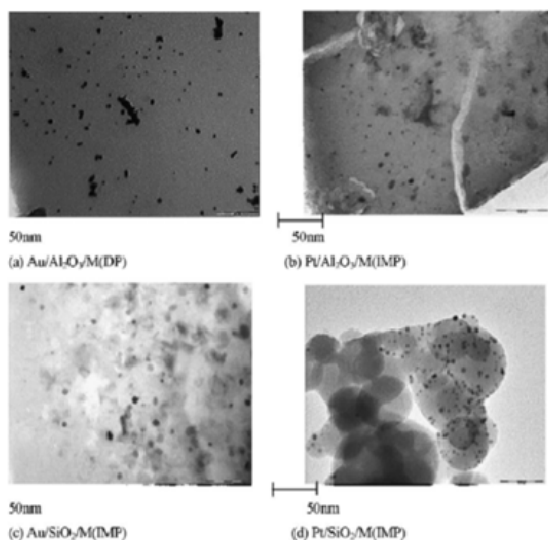


Figure 2. TEM Images of Commercial Catalysts

TEM photos in **Figure 2** show the resultant nanoscale platinum and gold formed via the metal salt method on a zeolite support. This catalyst is used in a stationary hydrocarbon-SCR application for the abatement of NOx.

QUANTUMSPHERE CATALYST STRATEGY

In contrast, QSI synthesizes nanometal particles prior to the introduction onto catalyst supports which results in greater control of the size and characteristics of the catalytic metal promoters. Referring to **Figure 3**, QSI nanometal particles have a metal core with oxide shell structure, as prepared by a patented vapor condensation process.

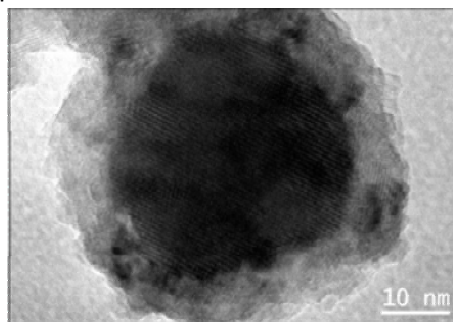


Figure 3. TEM Image of QSI Nanometal Particle/Oxide Shell

These nano-particles are then introduced onto support powders via dispersions (solid particles suspended in a liquid medium – usually water, and kept in suspension via dispersion agents) in very similar steps to current catalyst washcoat manufacturing processes. The result is finely distributed metal promoter particles on the targeted support powder (**Fig. 4**).

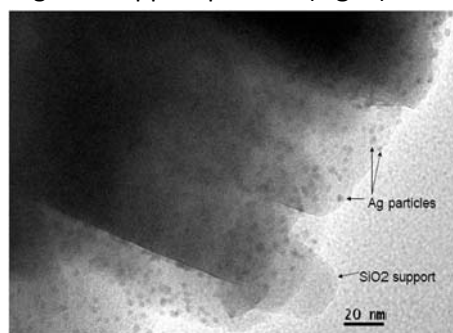


Figure 4. TEM Image of QSI Catalyst

The efficiency of emission control thermo-catalysis for a given nano-metal promoter and catalysis application largely depends on size (generally the smaller the better), location (on surface or more in the pore of the support) and nature of the nano-particle (raw metal or oxide).

RESULTS

The ability to fix the size and nature prior to introduction to the support powder, makes QSI's nano-metal promoters highly reactive, as shown in **Figure 5**, for a Three-Way emission control catalyst applied to a stationary CNG engine (lower bars refer to higher efficiencies).

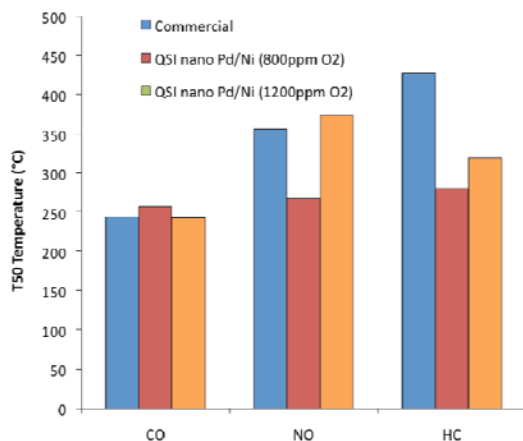


Figure 5. Conversion Efficiency of QSI Catalysts vs. Commercial Catalysts: T50 Refers to the Temperature at 50% Conversion of the Various Gaseous Species

Commercial refers to a commercial nano-catalyst that makes use of 35g/ft³ PGM loading at a PGM ratio of 6:3:1 (Pt:Pd:Rh), while the QSI's counterpart makes use of a 35g/ft³ QSI Pd/Ni alloy.

Note that the higher efficiency was obtained by effectively substituting nickel for rhodium, which is a huge cost saving. Also the nature and position of these nano-particles allowed the use of non-conventional metal promoters, in this case nickel.

The nature of QSI's nano-metal particles (metal core with thin oxide shell) also improve the high temperature stability of these particles, once fixed on the surface of the support powder. Normally the nano-metal particles agglomerate (come together) under high temperature conditions (>700°C) to form larger clusters of nano-metals, decreasing the overall surface area of the metal promoter available for catalysis. It is theorized that QSI's nano-oxide layer, gives extra strength to the *chemisorption* bond between the nano-metal particle and support powder, thereby

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lowering or eliminating this sintering pathway, maintaining its high efficiency rate.

Figure 6 gives an example of such stability during hydrothermal ageing (heating and introducing water vapor).

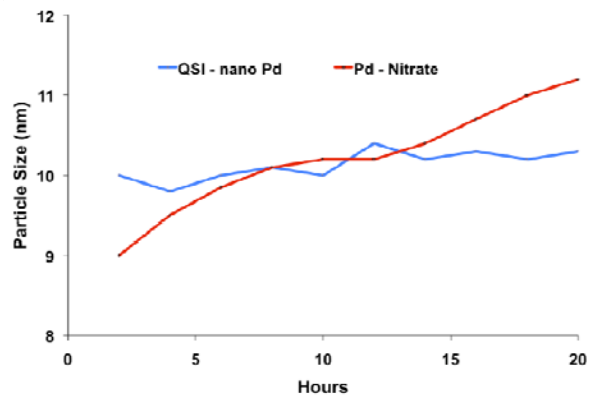


Figure 6. Particle Size Variation with Hydrothermal Ageing

The red-line indicates the particle size of the nano-metal promoter synthesized via the generic metal salts solution route, while the blue line indicates how the QSI nano-metal promoter particle size remains fairly constant throughout the 20 hour hydrothermal ageing cycle.

TEM photos in **Figure 7** also support this trend, as we see that the nano-particle synthesized via the metal salt solutions (red – Palladium nano-particles; grey – alumina support structure), start out as small clusters but during ageing (1000°C/ 8 hrs) agglomerate to create large sintered nano-Pd particles. This causes a decrease in catalytic efficiency.

In contrast, the QSI-Nano Palladium®(blue), deposited via a patented dispersion technology, retains its particle size distribution on the support powder (both samples make use of a standard alumina powder, 150 m²/g, average pore diameter of 15nm). This will ensure minimum agglomeration and thus greater retention of high catalytic efficiency at elevated temperatures.

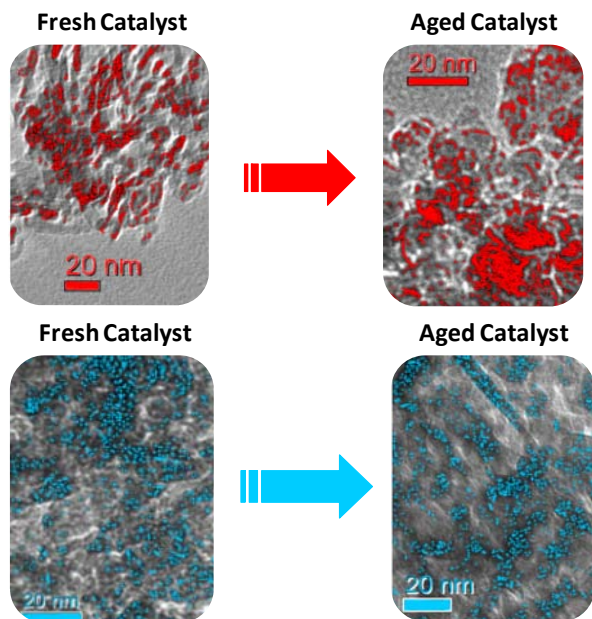


Figure 7. TEM Images of Commercial Catalyst (red) and QSI Catalyst (blue) Before and After Ageing.

CONCLUSION

QSI has developed a comprehensive range of nanoscale promoters that can be easily applied to emission control thermocatalysis. Advantages over the current commercial processes include:

- Greater control of promoter particle size
- Reduction in use of expensive precious metals by substitution with base metals
- Enhanced reaction efficiency
- Improved ageing characteristics.

Whether a DOC (Diesel Oxidation Catalyst), TWC (Three Way Catalyst), methane oxidation catalyst or similar, QSI has developed advanced technologies to overcome key challenges of the new decade; manufacturing, regulatory, and financial.

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About Dr. Fabrizio Rinaldi:

Dr. Rinaldi joined the QuantumSphere team in 2008 from Tenneco Inc, North America, where he held the position of Chief Engineer Emission Technologies for five years. His main tasks were the discovery and development of new emission technologies, tracking of emission regulatory and related drivers, as well as aiding Tenneco in catalysis issues both at a R&D and manufacturing level. He also represented Tenneco to MECA (Manufacturers of Emission Controls Association) both as a director and an officer. Prior to Tenneco, Dr. Rinaldi held various roles at Engelhard Corporation for over six years, both at the ETG (Environmental Technologies Group) divisions in Italy and in South Africa. The roles held were: Process Engineering Manager (SA), Director of Manufacturing (SA), Technical and Quality Director (Italy). Experience gained during these years ranged from the introduction of new catalyst technologies, wash-coat formulations, designing and developing and commissioning process machinery to directing manufacturing and quality operations.

During his tenure at Engelhard, Dr. Rinaldi headed the engineering and manufacturing that produced over 20 million units of catalyst-coated monoliths with a wide range of applicability, from gasoline three-way catalyst, diesel emission controls, to hydrogen recombination, and other specialty markets. Prior to the automotive emission world, Dr. Rinaldi was a senior research chemist for Karbochem, South Africa for more than four years. His primary duty was the R&D of specialty chemicals, from laboratory scale to pilot plant level. Chemicals investigated were: fuel additives, pharmaceutical intermediates, herbicides and pesticides. Dr. Rinaldi received a PhD in Organic Chemistry from UPE (University of Port Elizabeth), in Port Elizabeth, South Africa, under the subject: "Cyclizations of γ -Arylalkanols via Alkoxy Radicals and Aryl Radical Cation Intermediates." He currently holds two patents and has authored eight publications. Recognized as a leading authority in the emission control sector of the transportation industry, Dr. Rinaldi's work has been presented at several industry conferences/seminars around the world.