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An overview about Engelhard approach to non-standard environmental catalysis

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Abstract

The catalysis approach to clean air is a consolidated reality for automotive emissions and industrial stationary emissions, but a new world is opened for catalysis in non-standard emissions abatement. We report here an overview about Engelhard's approach to non-standard environmental catalysis. Emphasis is given to the need of a more flexible and customized approach to develop effective solutions at a cost that results in competitive products and services. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Engelhard's Environmental Technologies develops and markets sophisticated emission control technologies and systems that enable customers to cost-effectively meet stringent environmental regulations [1]. Over the past 40 years, due to the combined pushing force in emission abatement regulations and pulling force of our commitment to innovation as an established leader in catalyst technologies (Engelhard effort in R&D is as high as 60 ML$/Y), a series of highly advanced environmental technologies have been developed for abating noxious emissions from gaseous exhausts from either automotive or stationary sources.

Engelhard has found ways to help industries, governments, vehicle and automotive makers to comply with more and more stringent clean air regulations, which are ever increasing as worldwide concern for the deterioration in of air grows on a continual basis.

On the other hand, if catalysis approach to clean air is a consolidated reality for automotive emissions (including cars, motorcycles, bus, trucks and service vehicles) and industrial stationary emissions (including co-generation and gas turbine-based power generation facilities, biomass fired boilers, process industries, soil remediation applications) a new world for non-standard emissions abatement must be approached. There we need a more flexible and customized approach to deeply understand the technical issues of processes which we are facing with, market implications for our customers, all explicit and implied constraints, whatever is needed to offer our customers effective solutions. Moreover, this needs to be done at a price that results in competitive products and services for customers and markets they serve.

The complexity of problems, each of those being a "unique" case, needs deep expertise in surface chemical science, a strong team work and absolute trust among research and customers because of often needed exchange of confidential information. On top of that the ability to combine effectiveness, constraints

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and economics is needed together with updated and most innovative substrate materials which have to support the chemical work of catalyst.

The development of non-standard environmental catalysis, being often a niche market, although expected to rapidly grow in the future, requires thus an integrated effort between fundamental research in both catalysts and materials development and market- and customer-driven indications.

We discuss here selected applications of Engelhard non-standard environmental catalysis and technologies, showing the main critical aspects that lead to their development and the solutions that have been adopted.

2. Discussion

2.1. Automotive emissions systems

We spend a large portion of the Environmental Technologies Group R&D effort in this business segment. That is why Engelhard is the global market leader since 1970, with the fastest and most effective response to pollution control requirements. We have been able to anticipate and exceed regulations consistently. We serve both the OEM market and the Aftermarket with the widest range of solutions, even customized if necessary.

The special catalysts we present here are:

TriMax^{TM} *(trimetallic catalysts)*. This is a family of catalysts aimed to provide the lowest possible light-off temperature, so that emissions control is active within a few seconds as required by Euro 3. The proprietary washcoat based on three noble metals (platinum, palladium and rhodium) has as high flexibility as being a good starting point to comply with Euro 4. It results in outperforming the conventional TWC while offering outstanding resistance to poisoning, stable oxygen storage function and high temperature stability for close engine mounting.

HiTemp^{TM} *(close-coupled catalysts)*. It is an additional catalyst to be mounted close to the manifold. The purpose is to achieve a good enough start-up performance in converters with long pipe, when temperature loss is such a problem as preventing the catalyst from quickly reaching the right operative temperature. The ultra high temperature stability, together with a strong poisoning resistance, makes this additional catalyst able to provide the required performance during start-up of vehicle when installed in the high temperature area of the converter.

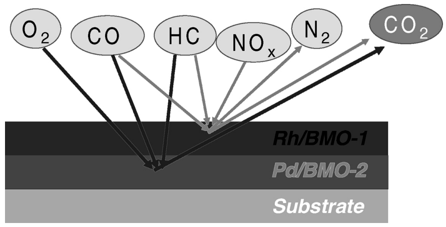

Fig. 1. Schematic drawing of the concept of segregated washcoats.

Segregated washcoat process. This proprietary washcoat allows atomic scale engineering of catalysts, which results in its fine tuning for sophisticated requirements. Precious metals can be atomically dispersed on specific base metals supports, avoiding formation of poorer performing alloys and compounds. Each precious/base metals specific washcoat is coated as an independent layer (Fig. 1). The layer at the interface with the offgas acts to reduce NO_x while facing an excess of reducing chemical species (CO/HC). The lower layer allows an effective oxidation step without any interference. Of course specific additives create an effective oxygen storage working strictly around $\lambda = 1$.

PremAir^{TM} *clean air systems*. This unique proprietary technology simply and effectively destroys ground-level ozone (when catalyst is coated onto vehicle radiators) (Fig. 2) or within airplane cabins. It is able to comply with the most stringent regulations (e.g. California). It reduces ozone created by other sources into oxygen directly when the car that has it installed is being driven, with an overall benefit for the surrounding environment.

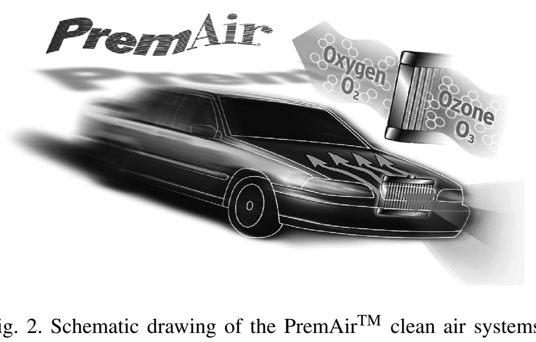

Fig. 2. Schematic drawing of the PremAir^{TM} clean air systems.

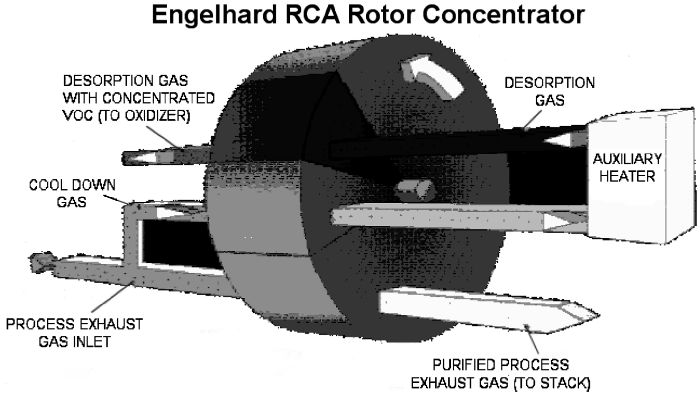

Fig. 3. Schematic drawing of the concept of zeolite rotor concentrators.

2.2. Emission and performance systems

The other large business area of Engelhard Environmental handles emissions from both stationary sources and vehicle (non-automotive) sources (e.g. two wheelers, heavy duty diesel engines, airplanes, small engines, forklifts, etc.). The products are grouped by emission type.

2.2.1. Carbon monoxide, VOCs or HAPs control

VOCat™ PTA. This, noble metals based, catalyst family is designed to abate pollutants generated during the process of purification of terephthalic acid, a key raw material to produce polyethylenterephthalate (PET). The volatile organic compound (VOC) most difficult to abate during this process is methyl bromide. These catalysts were specifically, but not exclusively, designed for the BP Amoco process.

VOCat™ 350 HC and 360 PFC. These, noble metals based, two catalysts were specifically designed to selectively abate both chlorinated and fluorinated VOCs (including dioxins and furans) producing the relevant halogenated acids, easy to be scrubbed during a further step. Amount of generated chlorine and fluorine, very nasty to be eliminated, is produced at lowest possible level.

VOCat™ 310 ST S and ST H. These, noble metals based, two catalysts provide effective VOC abatement in an environment rich in sulfur.

VOCat™ RCO. This is a, noble metal-based, catalyst family, designed to either retrofit or build up new regenerative oxidizers. It is useful to treat very large exhaust flows with a VOC total amount of more than 1 g/Nm^3. Those catalysts substantially lower operating costs of regenerative oxidizers with a quick payback period (often less than 1 year).

Zeolite rotor concentrators. This product family (Fig. 3) is aimed to optimize economics of either thermal or catalytic oxidizers (also regenerative ones). It is economically convenient to treat exhaust flows larger than 20–30,000 Nm^3/h and with a VOC total amount of less than 1–2 g/Nm^3. These concentrators safely and effectively adsorb and desorb VOC in such a way that 85–95% of the original flow rate can directly proceed to the stack, whereas a much lower flow rate, rich of VOCs, is sent to the oxidizer. The latter can, therefore, work with much lower operative costs. The payback period is very quick. Special hydrophobic zeolites are coated onto a fiber–ceramic honeycomb. The same technology—but with non-rotating panels—is used in VOC abatement for food service.

Camet™ CO oxidation catalyst. This unique catalyst, noble metal-based, coated onto a open cross flow channel (“herringbone” or “skew” type) corrugated metal foil, wound into monolithic structure, is the best available solution to abate CO from gas turbines exhausts (Fig. 4). It can be combined to the SCR catalyst below for complete exhaust abatement service and provides the lowest possible pressure drop with very high surface area. It is washable and non-hazardous when spent. The same technology can be used in several other VOC abatement processes (e.g. for appliances).

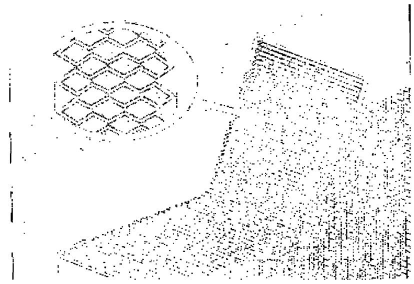

Fig. 4. Schematic drawing of the Camet™ CO oxidation catalyst.

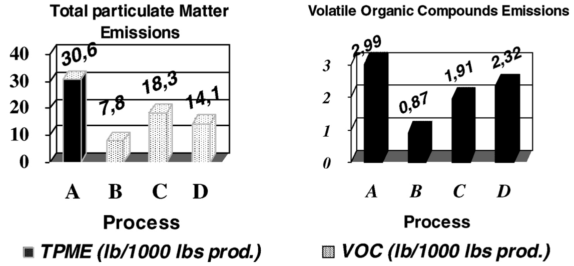

Fig. 5. Particulate matter and VOC emissions resulting from various solutions during cooking of a hamburger (see text).

CharCat 910™ catalyst. This catalytic system is designed to abate odours (VOCs) created in restaurant chain-driven charbroilers (Burger King). It is a device installed in the kitchen hood, which can be moved to the broiler's surface. Extra heating is not required, pressure drop is very low (the kitchen is working without forced ventilation) and maintenance is very easy.

Fig. 5 summarizes particulate matter and VOC emissions resulting from various solutions during cooking of a 24% fat hamburger. The worst one shows result of an untreated charbroiler. The best solution is the result of Engelhard continuous improvement over the previously established solution.

Odour abatement from ovens. This technology is used to abate odours both from household and restaurant ovens. Customized, noble metal-based, catalysts coated either onto ceramic or metallic honeycomb substrates are designed together with the customer. Fig. 6 sketches show some of chosen solutions.

The first one is the simplest arrangement to abate CO/HC. The extent of abatement depends on a number of parameters such as cooking temperature, space velocity, and noble metals loading. Catalyst is inside oven and no extra heating is required. The second arrangement is the appropriate one for complete abatement of both CO and HC either during normal cooking operations or during the pyrolysis step. External heating should be provided. Usually catalyst is installed within the extra heating device. The third equipment avoids external heating, but is more expensive, though very efficient. It is the solution of choice for rapid-cooking ovens (when a higher amount of odours per time unit is emitted). The last—more complicated—solution was studied together with Eisfink® (restaurant ovens) to combine pyrolitic VOCs destruction and adsorption, aimed to increase abatement efficiency. The adsorption panel is made of zeolites coated onto a fiber–ceramic honeycomb. It has to be externally regenerated once per day (a solution is under study to allow operation to be done without removing the panel). A demister is added to trap fat droplets.

2.2.2. NO_x abatement

NO_xCat™ VNX. This is based upon vanadia titania as the principal catalytic materials coated onto a cordierite (ceramic) substrate. The catalyst operating range is from 300 to 425 °C. Vanadia titania selective catalytic reduction (SCR) catalyst used are in

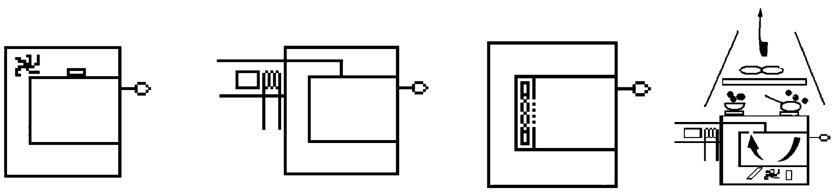

Fig. 6. Schematic drawing of different solutions for odour abatement from ovens.

numerous NO_x reduction applications, and have been successfully demonstrated in reciprocating engine, combined cycle turbines and utility/industrial boiler applications.

NO_xCat™ ZNX. This is a highly active, zeolite-based SCR catalyst designed to effectively abate NO_x in process industry and stationary engines (power generation) applications which have high discharge temperatures (ranging among 400 and 600 °C). This catalyst is also useful for nitric acid plants and in selected applications where N_2O abatement is required.

NO_xCat™ VNX-HT. This is a high temperature vanadia titania SCR catalyst. Designed specifically for aeroderivative simple cycle turbines used for peak demand. The operating conditions of these plants are much different than combined cycle plants in exhaust temperature, load cycle, operating time, vibration and temperature profiles during startup and shutdown. The catalyst has excellent activity and thermal stability with an operating range from 315 to 470 °C.

NO_xCat™ ETZ. This is a high temperature zeolite-based SCR catalyst designed specifically for large industrial simple cycle turbines which can have exhaust temperatures up to 610 °C. The catalyst is thermally stable up to 650 °C.

2.2.3. Particulate control

DPX™ soot traps. Catalyzed soot traps combine two advanced technologies—a precious metal catalyst and a ceramic soot filter—to remove harmful gases and visible soot from the exhaust of diesel engines. The trapped particulate is oxidized (a process known as filter regeneration) at 375 °C. Oxidation of CO and HC occurs at much lower temperatures and improves as temperature increases.

2.2.4. Other catalysts technologies

Hydrogen recombiner catalysts. This unique technology was studied for Siemens®. It is aimed to avoid explosion due to unwanted hydrogen release in the environment. For example, during severe accidents in nuclear power generation plants, the reactor core might start melting. Zirconium reacts with steam and hydrogen is formed. When 4.5% hydrogen in air lowest explosion level (LEL) is reached any hot spot or spark may ignite an explosive reaction between hydrogen and oxygen. Engelhard solution (several thin-walled stainless steel catalyzed metal plates, installed in a proper tray at the bottom of Siemens equipment) facilitates recombining of those gases, avoiding explosion and creating a strong buoyancy effect. Same technology is used to prevent explosion in several appliances (when rechargeable batteries are installed).

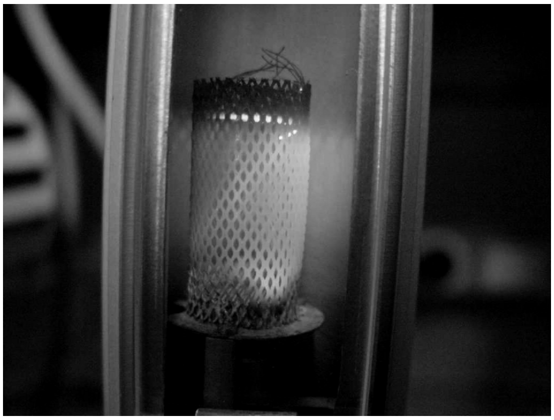

Fig. 7. A catalytic metallic net installed in the combustion chamber of hair-curlers.

Burner catalysts. These are again customized proposals to be studied case-by-case and always based on noble metals coating on different substrates. Among solutions (either under development or fully commercial) we would like to point out:

- A catalytic stainless steel net for residential heating burners.
- A catalytic ceramic honeycomb for camping devices burning propane.
- A device—similar to the above—installed in special mosquitoes traps, manufactured for places where many people meet together. Those traps burn propane to create a little environment rich in carbon dioxide. There, mosquitoes are attracted by special perfumes and get trapped.
- A device installed in hair curlers manufactured by Braun® (cylindrical metallic net, provided with several thin wires) (Fig. 7). It is installed in the combustion chamber where—after isobutane (stored in a little bottle under pressure) and air are properly mixed—piezoelectric ignition is provided. The wires are heated by micro-explosions and quickly transfer heat to the net.

3. Conclusions

This overview of Engelhard's Environmental Technologies activity within the area of non-standard environmental catalysis has briefly shown some of the market needs, but also the need of fundamental scientific research on new catalysts, materials and technical solutions in order to extend the application of catalysis to non-traditional areas.

Non-standard applications often require a more flexible and customized approach, and low per unit costs. Often they represent niche markets, but the extension of their use with clear environmental benefits requires that research is not only driven by customer needs, but is supported from a fundamental and interdisciplinary research (from surface science to catalyst preparation and engineering) which develops the scientific basis for future market applications.

Reference

[1] To read a summary of patents, scientific works and technical papers, www.engelhard.com/etg