

Executive summary

The basic research target of NEXT-GEN-CAT is the development of novel eco-friendly and cost efficient nanostructured automotive catalysts utilizing transition metal nanoparticles that can potentially replace partially or complete the currently used Platinum Group Metals (PGMs). The main concept of the project is the development of efficient catalysts by incorporation of low cost transition metals into different substrates, advanced ceramics, using updated nanotechnology tools. The synthesis and optimisation of various types of supports, promoters (CeO_2 , $\text{CeO}_2\text{-ZrO}_2$, Al_2O_3) and active phases (perovskites and metal/metal oxide nanoparticles) with exceptional mechanical and thermal properties, as well as improved oxygen storage capacity is crucial innovative aspect of the proposed work-program. Concerning the preparation of active, transition metal based automotive catalysts, several synthesis strategies evaluated including grafting, assisted and controlled impregnation, co-condensation, direct functionalisation, sol-gel/bio-silicification, modified polyol, wet chemistry, citrate methodology and flame spray pyrolysis have been developed and optimised. The developed materials were thoroughly characterised by conventional as by *in-situ* techniques and the mechanisms involved during materials' preparation were identified.

Modelling activities focused on the determination of bulk and surfaces electronic properties of the developed catalysts and to predict their final catalytic properties. The idea was to link experiments, ab initio estimations of pre-exponential factor and activation energies in a detailed kinetic model. The input of the modelling activities contributed significantly towards the optimisation of the developed catalysts. Furthermore, the activities on the simulation of the process and the operation of catalytic monoliths were focused on developing the reaction kinetics from the experimental tests and flow/transport simulation codes.

Overall more than 300 samples from various categories of materials namely silicas, silicon carbides, perovskites and doped perovskites were prepared and evaluated, using the protocols developed within the project. Regarding the evaluation of the materials realistic benchmarking scenario was applied for the assessment of the catalytic efficiency of the prepared catalysts. The samples were ranked according to their efficiency, upscalability and environmental impact. Using this ranking the consortium selected the copper doped CeZrO_4 and the copper doped LaFeO_3 as the most promising materials for the development of the prototypes.

The main exploitable result of the project was the upscaling of two most promising catalysts and the development of two prototypes, as after treatment systems. The consortium was also determined the performance of the developed prototypes according to the EU emission standards to justify the sustainability of the developed. In order to prove the viability of the developed after-treatment systems assessment of the complete life cycle of the developed TWC as well as on the definition of their end-life scenarios were performed. Thus the prospects of recycling the novel spent catalysts were thoroughly examined within the project and the environmental impact of the developed materials was determined by a Life Cycle Assessment (LCA) study. In all cases the developed materials exhibited lower environmental impact.

The obtained results apart from the scientific and technical progress bear significant environmental and economic impact. The reduction of automotive pollutants is in agreement with the EC directives (Euro 6) towards more strict regulations in automotive sector. On the other hand the reduction of PGMs in after treatment systems will secure the undisturbed supply of the European industry with critical resources, eliminating problems that can be faced in the future due to overexploitation or trade and political restrictions, strengthening the leadership of European companies in the automotive sector.

NEXT-GEN-CAT emphasised also on the dissemination of the obtained results towards the scientific community and the general public. The consortium participated to several conferences as well as published the

scientific results in in prestigious journals. The consortium was also organised the 1st Workshop on Critical materials in Catalysis: the case of automotive catalysis was held on 29th January 2016 at University of Lille and attracted more than 50 participants. Furthermore, the NEXT-GEN-CAT partners established concrete bilateral collaborations. Finally more than 17 master and PhD students as well as 20 post-doctoral fellows were trained and worked for the project, with a good gender balance.

Project context and Objectives

The main objective of NEXT-GEN-CAT proposal was the development of novel eco-friendly nano-structured automotive catalysts containing transition metal nanoparticles that can partially replace the PGMs, currently used in automotive after-treatment systems. Based on nanotechnology, low cost nanoparticles were incorporated into different substrates, including advanced ceramics (SiO_2 , perovskite, TiO_2 , SiC etc.) towards the development of efficient and inexpensive automotive catalysts.

Automotive after treatment systems, designed to detoxify the exhaust gases, went in production in 1975 in the US and until nowadays there is ample information available to conclude that these devices, which are the principal automotive emission control tools, have proved to be an undoubtable success. Following the positive experience in the US, in short order Japan and thereafter Europe, in 1986, adopted the use of automotive catalysts.

The field is driven by environmental issues whose aim is to mitigate the undesirable side effects of modern lifestyle. Personal mobility is considered an essential part of this lifestyle and has come to be viewed as almost an inalienable right. The national and international regulatory bodies enforce ever more stringent emission rules so that the field of automotive catalysis is perpetually at the very edge of technology.

The most common type of catalyst found on gasoline engines is the so called Three-way catalyst (TWC). The term 'three-way' denotes simultaneous catalysis of three different reactions (oxidation of CO into CO_2 , oxidation of HC into CO_2 and H_2O , reduction of NO_x into N_2 , CO_2 and H_2O). TWCs operate in a closed-loop system including a lambda sensor (also called oxygen sensor) to regulate the air-fuel ratio. On the other hand, vehicles equipped with lean engines, either diesel or gasoline direct injection engines, produce oxygen-rich exhaust, which prevents the reduction of NO_x via the "three-way" catalyst commonly used for stoichiometric engines. This means that, providing that the temperature is high enough, the oxidation reactions of CO and HC are both strongly favoured, but the reduction of NO_x is not. The new combustion and catalyst technologies (Selective Catalytic Reduction –SCR, NO_x adsorbers etc.) for lean engines must meet NO_x emission standards as well as those for carbon monoxide, hydrocarbons, and particulate matter (soot). For diesel engines, special exhaust filters have eliminated the unsightly plumes of soot emissions from diesel exhaust.

The traditional TWC is composed of an active phase (PGMs) supported on a honeycomb monolith made of cordierite ($2\text{MgO}_{0.2}\text{Al}_2\text{O}_{3.5}\text{SiO}_2$) or of PGMs covered by an alumina wash-coat doped with several elements (Ce, La, Ba) to ensure high specific surface area at high temperature and a good dispersion of the active phase. The active phase usually contains two noble metals: platinum and rhodium. A small quantity of rhodium ensures NO_x reduction and platinum is responsible for the total oxidation of CO and residual hydrocarbons. The wash-coat is often doped with varying concentrations of ceria, which plays an important role in oxygen storage and improves the dispersion of the noble metals. The role of ceria as an oxygen storage component is manifested by the ability of ceria-containing catalysts to store oxygen under lean operating conditions and release it under rich conditions by reacting with CO, hydrogen, or hydrocarbons. The working conditions of the exhaust catalysts are very harsh, with thermal shocks, humidity in the gas stream (ca. 10% water), and poisonous trace impurities such as sulfur, phosphorus, and/or zinc in the exhaust gas. These conditions decrease the lifetime of the catalyst either through direct poisoning or by sintering of the wash-coat and loss of dispersion of the active phase by sintering of the noble metals. The lifetime of the catalyst is also decreased by loss of the active phase, especially rhodium, because of solid-solid reactions with the wash-coat that result in the formation of surface or sub-surface spinel.

The choice of noble metals (PGMs) as the active catalytic materials in TWC is the result of three factors: (a) only the precious metals exhibit the activity required for the removal of the pollutants in the very short

residence times (large exhaust volumetric flows and small catalyst size due to small available space; (b) the precious metals are the only catalytic materials that can resist poisoning by residual amounts of sulfur oxides in the exhaust; (c) the precious metals are less prone (but not entirely immune) to deactivation by high-temperature interaction with the insulator oxides of Al, Ce, Zr, etc., which constitute the so-called high surface area “wash-coat” on which the active catalytic components are dispersed. While initially Pt and Pd in various proportions were used as oxidation catalysts, Rh was introduced with the advent of the three-way catalysts, having considerably better activity than Pt or Pd for the catalytic reduction of nitrogen oxides.

Noble metal catalysts are of particular commercial importance, and among these catalysts, palladium- and platinum-containing materials have recently received particular attention owing to their role as oxidation catalysts in automobile emission control systems as well as reforming catalysts for the production of high-octane gasoline. In Europe, the consumption of platinum for auto catalysts reached 1.415 million ounces in 2010, accounting for about 72.4% of the total platinum demands and about 68.2% of the total European palladium demand.

Over the next years, legislation will demand lower pollution levels from light and heavy duty engines and new regulations will be introduced to control emissions from other sources, such as ships and trains. Thus the future automotive catalysts will need to be more active, work at lower temperatures, respond rapidly to the change in operating mode of the vehicle, and remove pollutants as soon as the engine is switched on.

As PGMs are quite limited on earth, their effective replacement, partial or complete, with low cost transition metals in the automotive catalysts is of great importance and several scientific studies are focused on this task. The minimisation/ elimination of PGMs usage will secure the undisturbed supply of the European industry with critical resources, eliminating future problems, due to overexploitation or trade and political restrictions. The presence of copper, cobalt, nickel, iron and zinc in Europe even at small quantities as well as their worldwide occurrence, enable the secure flow of raw materials in our continent, strengthening the leadership of European companies in the automotive sector.

NEXT-GEN-CAT proposed an integrated approach on the preparation of innovative, low cost and highly effective nanostructured automotive catalysts based on the partial replacement of noble metals by transition metal nanoparticles (TMN). The proposal targeted on the development of a novel method for commercial (large-scale) preparation of nanostructured materials in the monolithic form, providing not only the research platform for their development but also the necessary engineering tools for their effective adaptation by the automotive after treatment industry. The approach used by NEXT-GEN-CAT project can be outlined in four main objectives:

1. Design and preparation of innovative nanostructured catalysts

The objective was the preparation and optimisation of various types of supports, promoters (CeO_2 , CeO_2 - ZrO_2 , Al_2O_3) and active phases (perovskites and metal nanoparticles) using transition metals towards the partial replacement of PGMs from catalysts used in the automotive field. Several synthesis strategies including grafting, assisted and controlled impregnation, co-condensation, modified polyol process, wet chemistry, citrate method and flame spray pyrolysis were evaluated and optimised. More specific the activities included the:

- Preparation of supports (SiO_2 , SiC, perovskites, TiO_2 , doped silicas)
- Preparation of actives phases (perovskites, doped perovskites, transition metal nanoparticles, bimetallic nanoparticles)
- The preparation of efficient catalysts with up to 45% reduction in PGMs used.

- Assessment of the effect of the various transition metals (mainly Cu, Ni, Fe, Mn and Co) on the catalytic properties of the materials

2. Nanoscale modelling

The objective was the development of theoretical models in order to simulate both the structure and properties of the nanostructured catalysts and to predict their final catalytic properties. A number of steps was required for the Modelling of the catalytic properties of a material i.e.:

- i. modelling the relevant surfaces of the material.
- ii. modelling the interactions between the surfaces(s) and the molecules of interest.
- iii. Devising possible pathways for the catalytic processes.
- iv. predicting the catalytic properties on the basis of the actual reaction pathways

DFT calculations of both the catalyst surface and the reaction mechanisms were performed over model to realistic systems. The key parameters that influence the activation energy and the rate determining step were identified. Furthermore, real time correlation of the theoretical results with experimental spectroscopic and kinetic data recorded under the conditions selected and were also performed within the duration of NEXT-GEN-CAT

3. Process optimisation

In the course of NEXT-GEN-CAT simulation codes were developed for the prediction of the performance of the real converters from the kinetics derived from the experimental tests. Kinetics proposed from ab initio studies for selected catalytic systems from were also incorporated in the simulation codes for prediction of the reactor performance. In the simulation codes reaction kinetics were coupled with mass transfer limitations and fluid flow characteristics to effectively calculate the performance of the catalytic systems in various dimensions. This method gave an insight of the fundamental mechanisms that participate in the catalytic conversion and guided the optimization of the catalyst shape, dimensions and rheological properties for the optimum catalyst preparation.

4. Materials Characterisation

Conventional techniques (Raman, SEM, TEM, AFM, BET, porosimetry, TPR, TPD) as well as “in situ” characterisation techniques (real time X-Ray diffraction) were applied for the physicochemical and structural characterisation of the nano-structured catalysts. This work will provided a better understanding on the way the scale and morphology of the metallic nanoparticles can promote synergistically high catalytic efficiency and thermal stability and contributed to the optimisation of the final materials. Furthermore, operando and in situ techniques provided information on (i) probing chemical functions with single molecules as CO and NO (ii) identifying adsorbed species, taking apart spectators and reaction intermediates using combined kinetics/real time operando FTIR spectroscopy (iii) qualifying the evolution of the active phase under various conditions i.e. XRD as a function of temperature, operando Raman of working catalysts

5. Materials Evaluation

The prepared catalyst samples were tested for their activity and deactivation studies were performed, always compared against the corresponding activity of a selected commercial catalytic converter. The catalytic tests were carried out in continuous flow tubular reactors at isothermal conditions and reaction rates were determined at different operating temperatures. Kinetic equations derived from the experimental data taking

into account the possible mass transfer limitations around the catalyst particles were used in simulation of the performance of the catalytic converters in full scale operation. The results of this study were assessed by the teams who were in charge of the preparation of the catalysts and provided guidance towards the modification and further improvement of the catalytic materials.

6. Upscaling – Development of prototypes - Evaluation of prototypes under real conditions

The main objectives included the selection of the most promising materials, their upscaled production, the preparation of the prototypes and their performance evaluation under realistic / ageing conditions.

Key activities undertaken were:

- Selection of the most promising materials using the evaluation protocols developed by NEXT-GEN-CAT
- Upscaled production by FSP or wet chemical routes of 2 selected samples to kilogram quantities
- Wash-coating of the upscaled samples onto commercially available monoliths
- Development of the 2 prototypes – after treatment systems
- Evaluation of the prototypes and the determination of their performance according to the European Emission Standards
- Determination of the noble and transition metal releases from the prototypes.

7. Recyclability – LCA studies

To safeguard the sustainability of the novel catalysts produced, it was essential to study beforehand their complete lifecycle and propose both environmentally benign and cost effective end-of-life scenarios. To this end the prospects of recycling the novel spent catalysts were thoroughly examined in this project. This recycling process in summary consisted of (i) dismantling of the catalyst, (ii) crushing and milling of the metal bearing substrate and (iii) recovering the metal from the substrate

Increased performance properties, cost reduction, longevity and low consumption of resources were the drivers for materials developed within NEXT-GEN-CAT. Furthermore, apart from the technical and economic factors, health and environmental parameters have also played a crucial role in the selection of the optimum replacement material. Finally safety, environmental compatibility and health risk assessment has been conducted for both the nanoparticles and the final products.

Description of main S & T results/foregrounds

WP1. Requirements and methodology for the preparation of the novel catalysts

The main objective of the WP1 was to define the requirements of the next generation of automotive catalysts, to identify the critical raw materials that are currently used in automotive after-treatment systems and to define the possible routes leading to the replacement of these critical raw materials. The main demands for this industrial sector were increased effectiveness, reduction in PGMs content and low cost of the new catalysts. In parallel, the developed materials should also exhibit: i) high recyclability ii) increased mechanical and thermal stability and iii) environmental / health compatibility.

The consortium initially updated the State of The Art for the TWC and determined the optimum replacement materials. The industrial partners concentrated on the latest developments on the field and how these advances could assist the project. On the other hand the academic partners investigated and updated the methodologies for the development of TWC by partial or complete substitution of the PGMs by transition metals originally presented in the proposal.

Based on the abovementioned, a roadmap was prepared, outlining the main scientific and technological approaches. The plan described the different preparation strategies, the techniques for the thorough structural and physicochemical characterisation of the novel catalysts, the simulation tools- both nanoscale modelling and process optimisation- that would be employed during the project for the prediction of materials' performance as well as the evaluation criteria for the assessment of the overall materials' performance.

Apart from the scientific methodologies, the consortium defined the strategies to be followed for the up-scaling of the most promising candidate materials as well as the plans for their recycling/regeneration. Furthermore, the participants defined the benchmarking scheme for both the initial materials and the final prototypes and the contingency strategy to overcome the expected technical risks (disadvantages, range of applicability, limitations etc.) associated with the main approaches set by the proposal.

The requirements were continuously reviewed and updated according to the progress and the latest external technical and economic developments in the field. Since WP1 was finalised before the end of the project, the proposed plans for the various sections of work during the project i.e. synthesis, characterisation, modelling, evaluation, up-scaling and assessment under realistic conditions were revised by the corresponding WPs. Towards a smoother implementation of the project the partners ranked the developed materials based on their catalytic efficiency, facile preparation route/up-scaling, cost and environmental impact. The selection of the materials that were upgraded to prototypes was based on this ranking.

WP2. Preparation of novel nano-structured catalysts

The objectives of WP2 were related to the synthesis and optimisation of various types of supports, promoters (CeO_2 , $\text{CeO}_2\text{-ZrO}_2$, Al_2O_3) and active phases (perovskites and metal nanoparticles) using transition metals aiming to partially replace PGMs from catalysts in the automotive field. The materials to be developed had to exhibit excellent dispersion of the active phase, improved catalytic efficiency together with low cost, increased thermal and mechanical stability, facile synthesis, up-scalability and low environmental impact.

Concerning the final goal of the project, i.e. the preparation of active transition metal based automotive catalysts, several synthesis strategies were evaluated within its duration. To this end, grafting, assisted and controlled impregnation, co-condensation, direct functionalisation, sol-gel/bio-silicification, modified polyol, wet chemistry, citrate methodology and flame spray pyrolysis have been developed and optimised. At the end, several of these methods were rejected as after initial investigation and optimisation they did not fulfil all of the criteria set in WP1 therefore lacking the potential towards their final application in automotive catalysis.

On the other hand, a few of these methodologies were selected for further optimisation and the corresponding materials were subjected to a more thorough optimization and characterization.

Aiming to employ a more eco-friendly and up-scalable method, the “ammonia-driven deposition precipitation” (ADP) methodology was developed and investigated within WP2. In concept, this method involves more eco-friendly reactants such as copper nitrate and water for the preparation of SBA-15 containing well-dispersed copper nanoparticles. Preliminary results of Cu loaded SBA-15 material prepared by this method, showed great potential towards the dispersion of Cu nanoparticles on the support surface. However, the presence of a small amount of poorly dispersed bulk copper affects the catalyst’s efficiency and durability. After several optimisation cycles concentrated mainly on metal loading and particles dispersability performed by UA, the latest characterization results indicated a significant improvement of the copper particles dispersion on the support material with a decrease of bulk copper on the surface. Additionally, a stronger interaction between the Cu nanoparticles and the support material was also observed. This interaction will suppress the mobility of the Cu nanoparticles on the support and thus inhibit their sintering at high temperature.

The optimisation of the ADP technique (by UA) involved also its successful transfer to a support more commercial available (such as γ -alumina) and to a bimetallic Cu/Ni system. Because of the superior hydrothermal stability of the latter support material, Cu/Ni loaded γ -alumina became one of the main research targets. Samples with varying ratios of Cu and Ni loadings’ were prepared and tested for their catalytic performance. The results revealed excellent catalytic conversion of CO and HCs (C_3H_8 and C_3H_6). Additionally, an increase of CH_4 and C_3H_8 conversion was observed at higher Ni content. On the other hand, the influence of the calcination temperature on the materials properties was also investigated. It was found that at higher calcination temperature the formation of bulk copper alumina becomes more significant. This is believed to have an effect on the materials catalytic activity. Recently it was observed that when the calcination temperature reached 850 °C, the well-dispersed CuO becomes the dominant species besides the copper aluminate alloy. The catalytic performance of this material will be tested in the near future in order to investigate in more detail the effect of the presence of copper alumina and well-dispersed CuO species.

Regarding the modified polyol methodology various approaches were attempted with several metal binding polymers tested for the impregnation of SBA-15 with the selected metals. Experiments conducted with the use of sodium alginate resulted in a final material with relatively low copper loading (below 2%). In an effort to surmount this problem and achieve a higher copper content, several routes were considered including the use of other chelating agents and the modification of the impregnation procedure. Based on these modifications the consortium (NCSR) was able to prepare silica based materials with controlled, tunable and predefined metal loading (up to 8 % Copper, down to 0.05% Pd). Furthermore, the modified polyol methodology enabled the in situ growth of bimetallic Cu-Pd NPs, either at the external surface or at the internal pore system.

In order to prepare supports with increased hydrothermal stability, the activities were focused on the preparation of novel nanoporous silicate materials containing metal nanoparticles by means of co-assembly and one-pot templating pathways and the production of copper loaded heteroatom substituted SBAs. The corresponding studies revealed that the most crucial synthesis parameters determining silicas’ pore architecture and morphology are the pH of the synthesis gel and the polymer’s molecular weight. More precisely, it was found that the one-pot pathway when conducted in a neutral pH environment with the use of higher molecular weight PEI enabled the production of copper loaded silica with advanced textural features, high copper content and excellent dispersion of copper species. Based on the knowledge gained from this work, research efforts were focused on the preparation of low content (below 0.1%) Pd loaded samples. For

this purpose, the optimum synthesis conditions were adopted and the obtained materials exhibited very good results in terms of pore structural characteristics, Pd dispersion and activity towards NO reduction by CO.

Research efforts related to copper loaded heteroatom substituted SBAs were devoted to the augmentation of Ce, La and Cu content in the final materials. In this direction, the pH-adjusting technique was modified by increasing the solution's pH and the amount of cerium and lanthanum precursors whereas post-synthetic methods such as incipient wet-impregnation (IWI) and excess solvent impregnation (ESI) were also employed as alternatives. Moreover, double promotion of ordered mesoporous silicas was accomplished by synthesizing Zr-Ce and Zr-La doped SBAs by means of an acid-free approach.

In addition, two novel hybrid sol-gel routes were employed as an alternative approach to the preparation of nanoporous inorganic structures functionalized with transition metal nanoparticles, using polymers either as biomimetic molecules or as a reactive template. The first method, biomimetic synthesis, resulted in the production of organic-inorganic nanospheres through interaction of hyperbranched polymers with silicic acid using sol-gel chemistry. Metal loading of the hybrid material was easily achieved due to the retained chelating properties of the hyperbranched polymer integrated into the silica matrix. After calcination, the obtained copper/silica nanospheres exhibited high metal loading of the order of 5-8 %, combined with enhanced copper dispersion, as indicated by XRD, EPMA, UV-vis DR and H₂-TPR results. However, N₂ adsorption experiments revealed very poor pore structural characteristics (ssa: 17 m²/g and TPV: 0.042 cc/g).

The second method involved the exploitation of hyperbranched polymers, both as a macromolecular porogen and a reactive template, forming covalent bonds with an appropriate silica precursor. The developed procedure included, dissolution of a hyperbranched polymer in different types of solvents and addition of 3-(triethoxysilyl)propyl isocyanate as a silica precursor, which is reactive towards the polymer's secondary and primary amino end groups. The obtained triethoxysilyl hyperbranched derivatives were subsequently hydrolyzed and cross-linked via the sol-gel approach, yielding nanostructured dendritic based networks. Template removal upon calcination resulted in nanoporous silicas with high surface areas and tailored pore structure. The effect of several parameters, such as the hyperbranched polymers' molecular weight and the type of solvent, were investigated in relation to the resulting silica network properties, with the aim of obtaining a more mesoporous material. Metal functionalization of nanoporous silica was accomplished either during synthesis (one-step synthesis) or through impregnation of the hybrid silica-polymer material into metal solutions (two-step synthesis).

Additionally, the consortium (NCSR) focused on the preparation of porous silicon carbide (SiC) / transition metal nanoparticles (TMN) composites using biopolymers as metal chelating agents. To this end, several novel synthetic approaches were applied. Non-solvent coagulation methodology was employed for the synthesis of SiC composites in the form of beads, using either chitin or alginate as metal binders. Furthermore, other synthetic approaches involved the preparation of an O/W emulsion and resulted in the production of monolithic samples and ceramics with oriented tubular pores. Pore structural characteristics of the precursors were enhanced by means of sc-CO₂ drying. In order to ensure reproducibility of the preparation methodologies, as well as to estimate the catalytic performance of final products with different active phases, several batches loaded with different metals (Cu & Ni) were prepared and characterized. Finally, efforts towards the optimization of the catalysts focused on an increased SiC/SiO₂ proportion in the final product. For this reason, a higher initial amount of SiC precursor (up to 65%) as well as several sintering procedures (different gases and final sintering temperature and heating rates) were employed and tested.

Regarding perovskite synthesis, hydrothermal methods have been used to synthesise a number of rare-earth free perovskites. This one-step method is desired for a number of reasons; it can be potentially scalable,

a calcination step is not required (unlike sol-gel and co-precipitation processes), agglomerate-free powders can be synthesised, morphology and composition can be easily controlled. Efforts focused on the hydrothermal synthesis of a number of titanates MeTiO_3 (Me = Ca, Sr, Ba), including incorporation of a number of redox active transition metals on the B site. The resulting perovskite materials were further characterized by XRD, BET and OSC techniques. The BaTiO_3 and SrTiO_3 materials had cubic structure and surface area of $15 \text{ m}^2\text{g}^{-1}$. Doping with transition metals resulted in phase pure perovskite materials ($\text{BaTi}_{1-x}\text{Me}_x\text{O}_3$) but with a limited doping amount depending on the transition metal; for example, cobalt was limited to $x = 0.2$ under the employed synthesis conditions. Above these doping levels, synthesis resulted in the formation of impurities such as cobalt oxide. The incorporation of these transition metals in the synthesis resulted in an increase of the unit cell parameters, indicative of lattice substitution. Furthermore, OSC was introduced into the perovskite materials above 300°C . Attempts to hydrothermally synthesise (one-pot) lanthanum based cobaltate perovskites have also been performed. Studies, involving both the nitrate and acetate precursors, varying pH, temperature and time and with various mineralizers, have failed, with the crystalline hydroxides of the precursors being the predominant product.

Flame Spray Pyrolysis was also employed for the preparation of perovskite materials. Initial work was on the synthesis of $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$ by FSP in which the resulting perovskite material was found to be phase pure with rhombohedral structure and a high ($\sim 60 \text{ m}^2\text{g}^{-1}$) specific surface area (SSA). Furthermore, the effect of the redox B site cation on the reactivity and stability of the perovskite was also studied, once again FSP was found to be a useful technique to synthesis high surface area perovskites such as $\text{La}_{0.9}\text{Sr}_{0.1}\text{MeO}_3$ (Me = Co, Mn, Fe, Ni). This study highlighted the advantage of Fe based perovskites for TWC reactions and therefore routes were taken to further optimise this material. The surface La/Fe composition was found to correlate with the light-off performance of FSP produced $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$ perovskite. Optimization of the La:Fe ratio in the precursor solution and type of Fe precursor allowed for a lower surface La/Fe content which resulted in optimized TWC performance. This optimized $\text{La}_{0.8}\text{FeO}_3$ catalyst was found to be comparable to a $\text{La}_{0.7}\text{FeO}_3$ prepared by the CNRS using the classic citrate method (CCM). This allowed for the transfer of optimized perovskite compositions prepared by small scale CCM to large scale FSP routes. Furthermore, $\text{La}_{0.8}\text{FeO}_3$ catalysts prepared by FSP were found to deactivate after high-temperature hydrothermal redox ageing due to sintering. Changes in the FSP process parameters allowed for the optimization of the particle size resulting in stabilization of the material against sintering under high-temperature dry conditions; however under the harsh hydrothermal redox conditions the deactivation due to sintering was not prevented.

Previous work carried out by JM had highlighted the potential of MnZr mixed oxides as a rare-earth element free support for PGMs and/or TMs. These mixed oxides could be used to 'buffer' the changing environment of the exhaust stoichiometry from rich to lean and allow oxidation reactions to continue under reducing conditions by supplying lattice oxygen from the surface of the mixed oxide component. Therefore collaborative efforts between JM and LURE focused on the transfer of MnZrO_x support synthesis to FSP. This novel approach proved successful for the synthesis of a high SSA MnZrO_x support which was later impregnated with Cu, Pd or Rh and was compared to a CeZrO_x reference prepared through standard precipitation routes. This work revealed a performance advantage of Cu/CeZrO_x materials for TWC due to a Cu-Ce synergy.

The consortium (CNRS) prepared nanostructured perovskite compositions (combining A- and/or B- site substitution + La-deficient materials + PGM doping) using the typical citrate method (CCM). Such compositions were further optimised through modification of the sol-gel procedure (Hydro-Alcoholic Method), including modification of the heat treatment conditions (temperature ramping, gas composition). This study provided new perspectives for continuation. Concerning the synthesis parameters, the optimization of the drying

conditions as well as the calcination parameters was pursued. Understanding the conditions influencing synthesis under stagnant atmosphere was the key for understanding the high catalytic activity towards NO reduction of the LaFeO_3 sample. A first step would be to investigate the calcination under humid and/or CO_2 -containing flow conditions. Furthermore, this method should also be extended to other compositions and solids. This transfer would allow further understanding as to whether the process is the same for different compounds. The final goal would be to establish a more easily up-scalable method. The most promising catalysts obtained by the composition optimization approaches were finally impregnated with low loadings of noble metals. It was shown that a reductive pre-treatment, lead to enhanced performance since the noble metals were present in their oxidic forms. Thanks to the high reducibility of the doped solid, the high intrinsic activity of the noble metals, a possibly segregated CuO phase, as well as the beneficial interactions with the perovskite support, marked increases in catalytic activity were obtained, especially for $\text{Rh/La}_{0.8}\text{Ca}_{0.2}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ and $\text{Rh/La}_{0.67}\text{Fe}_{0.83}\text{Cu}_{0.17}\text{O}_3$ yielding generally high CO and propylene conversions but also high NO reduction performance under rich and stoichiometric conditions

Some significant results concerning the CCM synthesized perovskites are summarised below:

LaCoO₃-based catalysts. Several samples were prepared substituting with Sr, Ba, and K. Covalent doping in A-sites should, in principle, increase the ionic mobility and thus the catalytic activity. The obtained results indicated that Sr-doping was the best choice in terms of structure stability, catalyst reducibility and catalytic activity. The more active catalyst is $\text{La}_{0.35}\text{Sr}_{0.35}\text{Co}_{0.5}\text{Cu}_{0.5}\text{O}_3$ in which higher reducibility and catalytic activity were observed, maybe due to the highly dispersed copper oxide.

SrTiO₃-based catalysts. $\text{Cu}_x\text{O/SrTiO}_3$, $\text{CoO}_x/\text{SrTiO}_3$, and $\text{Cu}_x\text{O/CoO}_x/\text{SrTiO}_3$ nanocomposites with Co/Ti and Cu/Ti atomic ratios were prepared by wet impregnation in water suspension of SrTiO_3 powder. The procedure developed (UNIPD) allowed the tuning of the particle dispersion and the oxidation state of Cu and Co.

Ruddlesden-Popper (RP) perovskites. Several compounds with and without La were prepared, characterized, and preliminarily investigated for the reactivity in CO oxidation and NO reduction reactions. The REE-free RP perovskites seemed to be poorly active in the desired reactions. Consequently the investigation focused on the La-containing catalysts: $\text{La}_{1.4}\text{Sr}_{0.6}\text{CuO}_4$ and $\text{La}_2\text{SrCu}_2\text{O}_6$ which showed interesting reducibility around 400°C. The comparison among the reactivity results allowed to conclude that in the CO oxidation the higher reactivity is shown by $\text{La}_2\text{SrCu}_2\text{O}_6 > 80\%$ conversion at 400°C).

Ni-based and Ni containing perovskites. Starting from LaNiO_3 several samples were prepared doping both in the A-site (with Ca) and in B-site (with Cu and Fe). The doping with Ca resulted in the formation of the Ruddlesden Popper structure. On the other hand, Cu-doping increased the reducibility of LaNiO_3 and its activity in CO oxidation. Furthermore, Ni containing perovskites, in which Ni is a dopant and the main B-species are manganese and cobalt were prepared.

Bi-based perovskites. In a new category of catalysts bismuth was used to substitute lanthanum. In order to stabilise the perovskitic structure Sr was used and the $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ perovskites were prepared. In addition to the structure stabilization Sr-doping also favoured the formation of the Mn(IV)/Mn(III) redox couple and thus the activity in redox reaction. Beside A-site doping with Sr also B-sites were doped with Ni, Cu, and Fe. The Bi-based perovskites were obtained with good purity; the presence of Bi, however seemed to be detrimental for the catalyst reducibility (TPR).

Barium manganate based perovskites. Several perovskitic catalysts were prepared starting from the magnesium doped barium manganate ($\text{BaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$); in these compounds both doping in A-sites (with Sr) and in B-sites (with Fe and Cu) were carried out. Fe caused a decrease of crystalline purity and of surface contamination whereas Cu and Sr enhanced the catalytic performance. In order to increase the catalytic

activity several nanocomposites were prepared depositing K_2O and NiO on the better performing Sr and Cu doped manganate, $Ba_{0.9}Sr_{0.1}Mn_{0.5}Mg_{0.2}Cu_{0.1}O_3$.

Ionic doping of perovskites (perovskite based nanocomposites). $LaCoO_3$, $LaNiO_3$ and $La_{0.5}Sr_{0.5}CoO_3$ were used as an active support for the preparation of copper oxide/perovskite nanocomposite catalysts ($CuO/LaCoO_3$, $CuO/LaNiO_3$ and $CuO/La_{0.5}Sr_{0.5}CoO_3$) in collaboration with UA. Several nanocomposites characterized by highly dispersed CuO nanoparticles were prepared in the compositional range 0-30 % wt. The prepared catalysts exhibited very good catalytic performance for CO and HCs, while the NO conversion was around 90 % at 350°C and the T_{50} around 270- 300°C.

Development of perovskite/monolith composites. Perovskite/monolith composites were also prepared following two procedures: the traditional washcoating and the direct synthesis, a procedure developed by UNIPD. The washcoating of a typical perovskite, $LaCoO_3$, on 450 cpi cordierite monoliths was investigated according to the traditional recipes (cycles of dipping and drying in a slurry). The resulting samples were compared with those obtained by the direct deposition/formation of the perovskite on the monolith via the citric acid sol gel method. The quality of the composites was investigated by XRD, XPS, SEM, and activity measurements. XPS and SEM indicated the minimum number of cycles to achieve a uniform coating. Additional cycles showed no further increase in catalytic activity. The traditional wash coating requires a significant number of cycles which increases the time and the labour involved while reproducibility could be an issue.

On the other hand, direct synthesis of the perovskite on the bare monolith in a single step through a sol-gel technique is a very promising process. The active monoliths prepared this way proved to be more effective than the wash-coated ones. Direct synthesis on the monolith is extremely simpler, faster and more reproducible. Finally, it is a sustainable process, without the use of organic solvents and can be easily up-scaled to industrial level.

Finally, since the wash coating is a very crucial parameter for the preparation of high performance catalysts, studies on the coating of the monolithic supports containing the nanoparticles synthesized previously were also performed. To this end, the consortium (TECNAN) focused on the synthesis of several catalytic promoters, such as CeO_2 , CeO_2-ZrO_2 , Al_2O_3 , etc., to be applied during preparation of the dispersions. These materials could act as the catalytic support and as catalytic promoters for the active materials produced by the other partners. On the other hand, Lurederra carried out wash-coating tests using both the promoters and the active nanoparticles synthesized by other partners (JM, UA, NCSR, UNIPD, CNRS). The wash-coating process involved: preparation of the suspensions (dispersion of the nano-particles), impregnation by immersion (dip coating) of the honeycomb monolith into the suspension and finally drying and fixation treatments (thermal treatments).

Overall in the duration of NEXT-GEN-CAT, for all materials categories, more than 300 samples namely silicas, silicon carbides, perovskites and doped perovskites were prepared and evaluated, using the protocols developed within the project. The samples were ranked according to their efficiency, up-scalability and environmental impact. Based on this ranking the consortium selected the copper doped $CeZrO_4$ and the copper doped $LaFeO_3$ as the most promising materials for the development of the prototypes.

WP 3 – Nanoscale Modeling

The modelling activities have been focused on the determination of bulk and surface electronic properties of perovskite using periodic density functional theory (DFT) at the GGA level, including on-site Coulomb interaction. Specifically, the PBE+U functional was used for all calculations in order to get accurate adsorption

energies of the reactive molecules on the surfaces. In order to model the molecules adsorption onto the surface, it was mandatory to get a good description of the solid electronic structures.

Two classes of perovskites were investigated: LaFeO₃ (LFO) containing La as rare-earth element, found to sustain a significant activity towards TWC and SrTiO₃ (STO), free of rare-earth elements, yet, when used as is, it gave a poor catalytic activity and needed to be promoted to be used as catalyst. The theoretical studies state of the art for STO and LFO materials was not equivalent. Indeed, the STO relevant surface had been well identified and documented whereas only scarce studies were devoted to LFO materials. LFO surfaces were, parenthetically, only devoted to the (010) LFO one, which was proven during the current project to be too energetic to be stable.

The DFT modelling of the activity of the LaFeO₃-based catalyst requires the successful fulfilment of the following steps:

- **The determination of the most stable and thus, the exposed surface(s) of the material.** In the case of SrTiO₃, the stable surfaces are those of the cubic structure whereas the surfaces exhibited by LaFeO₃ were demonstrated in the course of the project to be the (121) and the (100) ones.
- The evaluation of the **exposed surfaces stability in presence of water as a function of the temperature.** Reconstruction mechanisms were also investigated for supporting the previous step and definitely conclude on the surfaces stability. It was demonstrated that adsorption of water at 0K produced a significant change in the Wulff-constructed shape of the LaFeO₃ particle without changing the ranking of the most stable surfaces. Attempts to lower the LaFeO₃ (010) surface energy by reconstruction have definitively disqualified it as being a potential exposed surface of LaFeO₃.
- The depiction of **the potential active site(s) structure.** As expected, the DFT calculations performed have evidenced that the active phase is centered on Fe³⁺ cations.
- The analysis of **elementary reaction steps** (CO adsorption/reaction, NO adsorption/reactions) has made it possible to propose a **reaction mechanism** and provide activation energy values to be used as **input for kinetic modeling.**
- The investigation of the role of **doping elements** (Mn, Co, Ni, Cu) in the structure and the activation energies of rate-limiting reactions.

Concerning RE-free perovskite, the DFT modelling investigations focused on the formation of vacancies and other structural defects related to doping. The main results on doped SrTiO₃ materials during the NEXT-GEN-CAT project are summarized below:

- **Adsorption of relevant reactants on doped SrTiO₃.** Whereas on oxidized surfaces CO and NO are preferentially adsorbed at the impurity centres, on reduced surfaces they are attracted by the vacancy centres.
- **Catalytic oxidation of CO.** The rate-determining step for the catalytic oxidation of CO is the abstraction of surface oxygen by CO. The cost of this step is strongly reduced by cobalt-doping, which explains the enhanced catalytic properties of SrTiO₃ doped with this metal.
- Calculations on **NO reduction** over Cu- and Co-doped SrTiO₃ showed that: (i). the vacancy formation energy is a good descriptor for the catalytic activity, (ii) high density of vacancies is needed to obtain NO reduction to N₂. Furthermore, Cu-doped SrTiO₃ has been shown to be potentially very active for the NO reduction reaction.
- Calculations on the **faceted SrTiO₃ (110) surface**, a model to describe steps at the (100) surface, show that steps deeply modify the surface reactivity. At variance to flat surfaces, CO can be adsorbed not only at cation sites, but also at oxygen ones. Furthermore, several stable carbonate-type surface complexes can be

formed. In this context, Co impurities play a double role: on one hand, they stabilize oxygen vacancies; on the other hand, they slightly inhibit the formation of carbonate species. Overall, steps are not likely to contribute to the catalytic oxidation of CO because they promote the formation of stable carbonates species which inhibit CO₂ desorption, a key step in the reaction mechanism.

Preparation and characterization of model surfaces

Two approaches were followed for bridging the material gap between powdered solids and *ab initio* DFT modeling. The first one was based on preparing polycrystalline thin films of LaFeO₃, La₂CuO₄ and their derivatives after substitution in A/B or both sites. The strategy followed included the preparation of a precursor sol using a typical citrate route in the presence of ethylene glycol. This sol was then deposited on cleaned silicon substrates by spin-coating before undergoing calcination up to 650°C in air. Citrate/metal ratio, final metal composition of the precursor sol, viscosity and spin rate of deposition were among the parameters that were investigated. After optimizing the preparation, thin films retaining the perovskite structure -probed by XRD and Raman spectroscopy- showing only few cracks of average thickness not exceeding 300nm were obtained. The completion of this step has opened the way to advanced surface analysis of perovskite properties, including AFM, LEIS, and depth profiling using ToF-SIMS. The surface composition of the prepared films was checked using XPS so as to be comparable to that of conventional catalysts. The other approach was based on the preparation of monocrystalline layers of perovskite by epitaxial growth over selected monocrystals used as substrates (STO, MgO, LAO). Thus, perovskite films retaining a single orientation were successfully prepared using the pulsed-laser deposition (PLD) technique and fully characterized from the structural point of view. The potential of using non-linear optics based techniques (second harmonic generation and sum-frequency generation) for probing the outmost surface of solids was also explored on a model BaTiO₃ thin film.

WP4. Characterisation of the developed materials

The primary objective of WP4 was the physicochemical and structural characterisation of the nano-structured catalysts developed by the consortium within the project. To this end, conventional techniques (Raman, SEM, TEM, XPS, AFM, XRD, nitrogen porosimetry), high tech methods as well as *in-situ* or “operando” characterisation techniques (real time X-Ray diffraction) were applied for the thorough characterisation of the nano-structured catalysts. The obtained results provided a platform for better understanding the way scale and morphology of transition metal nanoparticles can promote synergistically high catalytic efficiency and thermal stability.

Based on the DoW and decisions made by the consortium, the developed materials were classified into four categories, namely, silicon oxides, silicon carbides, perovskites and oxide-based nanocomposites. For each type of material certain characteristics were required. In order to thoroughly investigate the properties of the developed materials, special groups of techniques together with advanced combination methodologies – operando techniques - were applied for every material.

The applied techniques provided details on the structural and physico-chemical properties of the materials. They also enabled the consortium to determine the surface properties and composition of the materials and gave information on the presence of impurities as well as the materials’ transition metal loading. Special care was also given to the evaluation of the materials stability under realistic conditions of temperature and humidity. Furthermore, the application of specific techniques available within the consortium also enabled the

determination of the properties specifically related to the materials catalytic efficiency, including redox properties, metal nanoparticle dispersion and oxygen storage capacity.

Apart from the prepared samples physico-chemical properties determination, WP4 also aimed to investigate the mechanisms of processes taking place during the materials preparation. This study was very important especially during the materials optimisation task. In addition, the correlation of structural and surface properties with catalytic activity enabled the preparation of materials with the desired efficiency and the investigation of the reacted catalysts allowed for a thorough study of the deactivation mechanisms. Furthermore, real time measurements allowed to monitor the evolution of the active phase under various conditions i.e. XRD as a function of temperature, operando Raman of working catalysts, providing information about the aging and deactivation processes. The consortium (CNRS) applied also in-situ IR in order to investigate the adsorption of CO and NO on layer of LaFeO₃ deposited onto a Si wafer, under vacuum. Based on the obtained results the chemical interactions between catalysts and single molecules (such as CO and NO) as well the identification of the adsorbed species were determined. Finally, in order to tackle the structure-activity relationship in La_{1-y}FeO₃ catalysts, in situ Raman experiments were carried out along with a sequence of model conditions (CNRS): catalysts activation, re-hydration under a controlled partial pressure of water and reaction under CO/He and NO/He fluxes. Two samples were compared: the stoichiometric LaFeO₃ (LFO) perovskite and La_{0.67}FeO₃ catalyst. A subsequent in-depth data analysis was performed and an original description of the evolution of catalysts surface when submitted to model conditions was proposed.

WP5. Evaluation of catalytic performance / Process optimisation

According to the DoW, two were the main objectives of WP5: (i) the performance evaluation of the developed materials and (ii) the simulation and the optimisation of the process.

Prior to the evaluation of the samples' activity the consortium agreed to a protocol to be used by all partners. The protocol, apart from the experimental conditions -temperature (up to 500°C), space velocity (60000h⁻¹) etc.- defined also the reactor type, the catalyst and inert particle size, the catalyst mass and the catalysts pre-treatment procedure. A reference catalyst wash-coated onto a cordierite monolith was provided from Johnson Matthey and was tested for its activity following the conditions specified in the experiment protocol. This sample was used as reference for the results obtained by each team during the implementation of the project.

Regarding the catalytic performance evaluation of the synthesized materials more than 250 samples have been tested by the consortium (NTUA, CNRS, UNIPD and JM). The majority of the samples, exhibited increased oxidation efficiency, while only a limited number (~30) showed acceptable NO reduction. Among the catalysts tested by NTUA, the SBA-Pd catalysts exhibited higher activity towards both NO reduction and CO oxidation as well as for oxidation of organic species. The SBA-Pd-Cu and SBA-Cu catalysts were active only for CO and C₃H₆ oxidation. Moreover, SiO₂-Ni-Cu and SiO₂-Fe-Cu also exhibited high CO and C₃H₆ oxidation activity while the ADP prepared Cu-SBA catalysts showed similar activity reaching total CO, C₃H₆ and about 90% C₃H₈ conversion. On the contrary Cu/ γ -Al₂O₃ catalyst exhibited lower activity with lower conversions and higher light off temperatures.

According to the tests performed by UNIPD, the most promising perovskites were the La_{0.5}Sr_{0.5}Co_{0.5}Cu_{0.5}O₃ and LaNi_{0.7}Cu_{0.3}O₃ as their T_{50s} were all below 350°C. Catalysts with T₅₀ less than 450°C, such as LaCoO₃+10% Cu, LaCoO₃+15% Cu and La_{0.35}Sr_{0.35}Co_{0.5}Cu_{0.5}O₃ for La-Co compounds, La_{0.75}K_{0.25}Mn_{0.7}Ni_{0.3}O₃ for La-Mn family, LaNiO₃ + 15% Cu, LaNiO₃ + 30% Cu and LaNi_{0.7}Fe_{0.3}O₃ for La-Ni perovskites, could also be considered acceptable.

The samples prepared at UA with different Cu loadings (10 and 15%) deposited on top of LaCoO_3 were found to enhance NO reduction in rich conditions compared to LaCoO_3 , but this improvement was not proportional to the Cu loading. The sample with 10% Cu was found to be the most active of the set for NO reduction. Furthermore, Ba doping and Sr sub-stoichiometric doping of La-Co perovskites replicated the behavior of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.5}\text{Cu}_{0.5}\text{O}_3$, and gave quite good results.

On the other hand, analogous samples (10 and 15% Cu loading) prepared at the UA on LaNiO_3 appeared interesting for the CO oxidation but did not have positive effects on NO reduction compared to LaNiO_3 , contrary to what was expected. Instead, Fe doping of LaNiO_3 required higher temperatures than LaNiO_3 to achieve good conversion of reagents, especially in rich conditions. Finally the La-Mn doped perovskites with alkaline promoters (Sr in sub-stoichiometric quantity and K) did not provide much better results than $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.7}\text{Cu}_{0.3}$, neither under stoichiometric nor under rich conditions.

University of Padova studied the preparation of perovskites by direct synthesis (DS) on the monolith and washcoating (WC,) for LaCoO_3 . Generally, La-Co based perovskites show a good oxidation activity, especially for CO. $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.5}\text{Cu}_{0.5}\text{O}_3$ and $\text{LaCoO}_3\text{-CuO}$ were picked out as very promising catalysts both for oxidation and reduction. La-Mn doped perovskites were in general less active than La-Co. CO oxidation by La-Ni compounds was slightly lower than that of the La-Co group, while activity towards hydrocarbon oxidation is comparable, and NO reduction was higher. REE-free materials such as $\text{Ba}_{1-x}\text{Sr}_x\text{Mn}_{1-y-z}\text{Mg}_y\text{Cu}_z\text{O}_{3-1}$ with different doping showed quite good activity, both for oxidation and reduction, but at higher temperature than the other cited materials.

A number of base metal and low PGM containing catalysts have been evaluated by JM for their ability to catalytically oxidize CO/HC and reduce NO, both under the NEXT-GEN-CAT testing protocol and the more realistic testing conditions typically employed by JM where gas conditions are cycled between rich and lean every 3 seconds.

The effect on the TWC activity and structural stability, of the B site cation in $\text{La}_{0.9}\text{Sr}_{0.1}\text{MeO}_3$ (Me = Co, Mn, Fe, Ni) perovskites prepared by FSP, was studied. Evaluation according to the NEXT-GEN-CAT protocol revealed the following trend in oxidation ability (T_{50} for CO given) under Stoic conditions: Co (280°C) > Mn (360°C) > Fe (380°C) > Ni (420°C). However, only the $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$ perovskite was able to reduce NO reaching >50% conversion and a $T_{50} = 420^\circ\text{C}$ under rich conditions in the 110-500°C temperature range. Furthermore, $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$ was found to be structurally unstable under harsh ageing conditions (hydrothermal redox conditions at 950°C for 20 hours), resulting in phase segregation compared to $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$ perovskite which remained structurally intact. This study highlighted the advantage of Fe based perovskites for TWC reactions and therefore routes were taken to further optimise this material. The surface La/Fe composition was found to correlate with the light-off performance of FSP made $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$ perovskite. Optimization of the La:Fe ratio in the precursor solution and type of Fe precursor allowed for a lower surface La/Fe content which resulted in optimized TWC performance. Under realistic perturbed JM testing conditions this resulted in a CO/NO light-off temperature improvement by up to 100°C and up to 30% in conversions at 500°C. This optimized FSP $\text{La}_{0.8}\text{FeO}_3$ catalyst was found to be comparable to a $\text{La}_{0.7}\text{FeO}_3$ prepared by the CNRS using the typical citrate method (CCM) under realistic perturbed JM testing conditions and met the requirements of the NEXT-GEN-CAT protocol. This allowed for the transfer of optimized perovskite compositions prepared in the small scale via CCM to the large scale FSP routes. This FSP prepared $\text{La}_{0.8}\text{FeO}_3$ perovskite material constituted the input to WP6 for scale up by LURE. Although $\text{La}_{0.8}\text{FeO}_3$ perovskites were found to remain structurally intact after harsh ageing conditions, their TWC performance was greatly affected due to sintering. Changes in the FSP process parameters allowed for the optimization of their particle size, resulting in stabilization of the material against

sintering under high-temperature dry conditions; however under the harsh hydrothermal redox conditions the deactivation due to sintering was not prevented.

A number of Cu containing and CuO supported materials were also prepared and evaluated by JM. The outcome of this study clearly highlighted an advantage with Ce-containing materials as supports due to a Cu-Ce synergy promoting both CO oxidation and NO reduction reactions. A Cu loading study on CeZrO_x revealed an optimum of 2 wt% Cu which was found to meet the NEXT-GEN-CAT target, even after high temperature hydrothermal redox ageing. Comparisons were made to other Cu containing materials prepared by UNIPD (La_{0.5}Sr_{0.5}Co_{0.5}Cu_{0.5}O₃), UL (La_{0.8}Ca_{0.2}Fe_{0.8}Cu_{0.2}O₃), NCSR (Cu/Al-SBA-15) and LURE (2Cu/MnZrO_x). Under both the steady state NEXT-GEN-CAT protocol and the perturbed JM conditions, Cu/CeZrO_x showed an advantage over the other materials with CO light-off temperatures comparable to a PGM catalyst and NO conversions >50% at 500°C. All other Cu containing materials from the other partners were found to not meet the requirement of >50% NO conversion at 500°C under the perturbed testing conditions. This Cu/CeZrO_x material was therefore outputted to WP6 for scale up and evaluation in the prototype.

The catalytic performance of stoichiometric and undoped perovskite solids (lanthanum iron/manganese/copper derived catalysts - CNRS) was first investigated and mainly underlined the stability of LaFeO₃ whereas the Ruddelsden Popper La₂CuO₄ catalyst exhibited the highest catalytic performance. However, complete decomposition of the Ruddelsden Popper La₂CuO₄ catalyst after one cycle in rich conditions was observed. The partial substitution of iron with copper (LaFe_{1-x}Cu_xO₃, x up to 0.2) led to a more stable catalyst and similar CO oxidation conversion profiles to La₂CuO₄. The partial substitution of lanthanum with calcium can be used to reduce the rare earth content for La_{1-x}Ca_xFe_{1-x}Cu_xO₃ with x up to 0.2 (CNRS). The change of the LaFeO₃ textural properties (“hydroalcoholic method”; “Macro-structuring method” - CNRS) did not lead to a significant improvement of its oxidative properties. Textural properties could be improved by optimizing synthesis parameters such as the employed solvent and the calcination atmosphere. The NO_x reduction performance improvement was obtained by changing the calcination atmosphere during LaFeO₃ synthesis.

The characterization of non-stoichiometric La_{1-x}BO₃ confirmed the possibility to tune the surface composition by decreasing the lanthanum content during synthesis (CNRS). Surface composition optimization, i.e. lowering of the nominal La-content in LaFeO₃, resulted in higher accessibility of catalytically active iron sites on the surface of the perovskites. The combination of surface and bulk composition optimization for La_{1-x}FeO₃ and La_{1-y}Fe_{1-x}Cu_xO₃ catalysts led to significantly enhanced catalytic performance especially in the case of lanthanum-deficient synthesis. CO oxidation enhancement was more intense leading to catalytic performance similar to the reference catalyst in both stoichiometric and rich conditions. Furthermore, increased N₂ selectivity was observed compared to the commercial reference catalyst. The La-deficient synthesis strategy was also applied in CNRS for the partial substitution of lanthanum with calcium (La_{0.6}Ca_{0.2}Fe_{0.8}Cu_{0.2}O₃) but the expected enhancement was not observed for all reactions. Doping with low PGM content was then investigated. In the absence of pre-reductive thermal treatment, the addition of PGMs (Platinum, Rhodium or Palladium) showed a beneficial effect only after one complete cycle including rich conditions. On the other hand, pre-reductive thermal treatment of the 0.1wt% PGM sample, enhanced oxidation reactions as well as NO reduction. Among the PGM, rhodium doping (0.1wt%Rh/La_{0.8}Ca_{0.2}Fe_{0.8}Cu_{0.2}O₃ - CNRS) led to the highest NO conversion level. PGM doping was also investigated for Lanthanum-deficient synthesis. The influence of differences in the activation procedures was examined on the 0.1wt%Rh/La_{0.67}Fe_{0.83}Cu_{0.17}O₃ catalyst. Clearly the addition of rhodium improved NO reduction leading to catalytic performance similar to that of the commercial TWC solid.

Regarding the monolith evaluation, all $\text{CeO}_2/\text{ZrO}_2$ (50%w/w), SBA-15-Cu 5% and $\text{La}_{0.8}\text{FeO}_x$ 8% monoliths showed fairly low activity. Additionally, the PGM-free monolith exhibited low activity compared to the Low PGM monoliths. On the contrary, low PGM monoliths exhibited high activity comparable to that of the commercial monolith. Although there were some differences in the activity of the two samples, probably deriving from different wash-coating of the catalytic material, both samples were active. On the other hand, for the low PGM prototype tested by Monolithos in real exhaust emissions of a car engine, no deactivation was observed

The activities on the process simulation and catalytic monoliths operation were focused on developing the reaction kinetics from the experimental tests and flow/transport simulation codes. Ab- initio kinetics proposed in the literature for automotive converters have also been incorporated in the simulation codes for the prediction of the reactor performance. Furthermore, in the simulation codes including reaction kinetics mass transfer limitations and fluid flow characteristics were taken into account.

A 1 D kinetic simulation code was verified with published detailed kinetic data and different simulation codes. Three different detailed reaction mechanisms have been introduced to the code and have been tested, one for methane partial oxidation and two for conventional automotive converter experimental data. The mass and heat transport effects as well as diffusion effects were taken into account according to each catalytic system described.

Preliminary simulation of the laboratory activity tests for the Pd/Rh JMJ catalyst was performed by using the two different reaction mechanisms for Pt/Rh and Pt automotive converters with the simple PFR model, in order to compare their performance. In addition, the bimetallic reaction mechanism for Pt/Rh TWC was also used by the developed 1D isothermal kinetic model to simulate the performance of a real monolithic converter. The effect of different working conditions on the abatement of the automotive exhaust gases was studied.

Furthermore, a detailed 3D CFD model for the simulation of monolith steady state behaviour was developed using lumped kinetics and coupling momentum, mass and heat transport PDE's. Species concentrations, velocity and temperature profiles along the monolith channel can be calculated. CO oxidation along the monolith channel was tested as a case study.

The detailed 2-D CFD model for the CO oxidation at isothermal conditions along the monolith channel was developed in Comsol Multiphysics for the estimation of the mass transfer coefficients according to the two film theory, by using lumped kinetics, including also momentum and mass transport. The calculated mass transfer coefficients were validated by developing an isothermal PFR model coupled by the introduction of effective mass transport coefficient for each component. A constant mean value of the mass transfer coefficient along the monolith channel, or effective mass transfer coefficient as a function of length, was estimated and introduced to the 1-D isothermal model using detailed reaction kinetics. A simplified PFR model was developed to be compared with the detailed one.

The study of the mass transfer limitations showed that mass transfer affected the operation of the catalytic structure when the reaction rates were fast as well as when strong inhibition was included in kinetics. For relatively slow reaction rates the effect was not important. Using an effective mass transfer coefficient as function of the channel length the process could be successfully simulated and the predictions were the same as those with the detailed 2-D CFD model.

Reaction sensitivity analysis with respect to activation energy was performed on the published Pt mechanism applying the isothermal PFR model at the protocol conditions and 60000 h^{-1} GHSV. The activation energy was modified by $\pm 50\%$ for the reactions concerning all species but the hydrocarbons. A simplification on the reaction mechanism could be considered by determining the hydrocarbon reaction rates from lumped

kinetic equations (technical kinetics), so the reactions considered finally for the sensitivity analysis were thirty four out of seventy four included in the mechanism.

The simulation results for the abatement of the major pollutants (CO, C₃H₆, CH₄, NO) from the reaction sensitivity analysis were compared to those obtained previously under the same conditions, which simulated the kinetic laboratory experiments, where an isothermal packed bed of crushed JMJ TWC particles was tested.

Finally, only seven (7) reactions proved to be not sensitive to activation energy variation. For those reactions the simulation results for all the main species (CO, NO, C₃H₆, CH₄) were close to the standard ones for all modifications imposed at the three gas exhaust compositions.

Most of those reactions exhibit low activation energies indicating easily performed reactions, while in two cases their reverse reactions have very low sticking coefficients. However, the reactions with very high activation energy compared to the others included in the mechanism, proved also not to be affected by the 50% variation in the activation energy's value.

Simulations concerning only the rich gas feed composition, showed that eighteen (18) reactions were not sensitive, most of them being also associated with oxygen coverage or with oxygen adsorbed on the Pt surface. This suggests that as far as the Pt/Al₂O₃ mechanism is concerned, the presence of oxygen in the exhaust gas has more pronounced effect to the simulation results than the actual value of activation energies. This finding is attributed to oxygen and carbon monoxide coverage dependency of the kinetic data, affecting several important reactions of the mechanism.

Concerning the optimization of the technical kinetic models, a power-law and a Langmuir-Hinshelwood one were developed. The kinetic parameters were estimated achieving the optimal fitting to the experimental conversion data derived from experiments involving the two low PGM small monoliths which according to the activity tests was the most active monolith delivered and prepared for the needs of this project by other teams.

Both kinetic models fit satisfactory to the experimental conversions of the participating chemical species. The increase of NO conversion with temperature at higher temperatures and rich composition was in contrast to the corresponding experimental data derived for the stoic and lean feed composition and was attributed to the large inhibition effect of O₂ on the C₃H₈ steam reforming reaction to CO. Thus the steam reforming reaction of C₃H₈ takes place under O₂ absence conditions.

The performance of commercial size automotive converter was simulated at real operating conditions, running a detailed non-isothermal 2D CFD model and using the Langmuir-Hinshelwood technical kinetic model derived from isothermal experiments with both PGM small monoliths delivered.

Developing a 2D non-isothermal PFR model and comparing the results with those derived from the detailed 2D CFD model at the same conditions, it was concluded that the real automotive converter performance is limited by the external mass transfer effects at higher temperatures, which especially affect the NO and C₃H₈ outlet conversion for the rich feed composition. The PFR model resulted in more steep conversion and temperature profiles along the monolith for higher inlet temperatures in comparison to the detailed one, because the mass transfer effects in the detailed model are stronger.

An almost total conversion of CO and C₃H₆ was calculated at monolith inlet temperature 300 °C for all the conditions tested. Small NO conversions were calculated for lean and stoic composition lower than 20%. Higher NO conversions were calculated for the rich composition reaching 90% for the lower GHSV=30000 h⁻¹ and higher inlet temperature 400 °C tested. C₃H₈ starts to react at temperatures higher than 250 °C. The maximum C₃H₈ conversion was calculated at 54% for lean feed composition, 48% for stoic feed composition and 90% for rich feed composition, at GHSV=30000 h⁻¹ and for 400 °C inlet temperature. The maximum temperature

increase along the real automotive converter was calculated 119 °C, 96 °C and 70 °C for the lean, stoic rich feed composition respectively.

Detailed surface mechanisms and the corresponding micro-kinetics rate laws are strictly dependent on the catalyst nature and on its physico-chemical properties, including noble or platinum-group (PGMs) metals content. Based on the NEXT-GEN-CAT expectations, among all the catalyst developed during the project, those identified as the most promising, in terms of activity and selectivity would require a specific investigation of their kinetics.

To identify the kinetics, a reactor model had to be developed and fit to the experimental data, tuning the parameters in the rate law(s). This model would have to explain the transient hysteresis behavior typically occurring during temperature ramp-up and ramp-down experiments, carried out to monitor the catalyst activity. To perform the kinetics study the partners formulated a pseudo-1D model, deemed to employ the minimum level of detail to describe the problem. Since the NEXT-GEN-CAT project focuses on the automotive application, the model was developed for monoliths.

In the case of monoliths, it sufficed to model a single channel, assuming that all the channels behave similarly. The pseudo-1D model assumption described the gas phase as plug-flow, but it allowed for a different composition and temperature between bulk and near the catalytic wall, below the massive and thermal boundary layer. In this sense, it is a pseudo-1D, because it accounted for a simplified radial gradient of both temperature and species concentration quantified by means of specific heat and mass transfer coefficients.

The model allowed for any thermal behavior even though, especially at very low reagent concentrations, single channels can be reasonably assumed to behave adiabatically. The model included an energy balance for the solid phase, allowed to account for the thermal inertia of the solid phase (the catalyst support). The heat capacity of the solid allows for a decoupling of the gas and solids temperature, especially when elevated HR was used. Also, the model described the temperature profiles better, (along the flow/axial direction) both at the catalyst surface where the reaction actually took place and in the gas phase where the temperature was experimentally recorded.

The model assumed dynamic operation of the reactor, which was consistent with heating/cooling, such that the gas temperature at the catalyst inlet followed a defined heating/cooling rate policy. Moreover, the assumption of dynamic operation was also consistent with the procedure applied in carrying out the oxidation experiments and was more realistic compared with the assumption of a steady-state operation.

In case of continuous heating and cooling stages, the transition to the steady-state (both thermal and chemical) must be fast enough compared with the heating/cooling rate. This was not obvious (neither using sufficiently small heating/cooling rate), especially when the thermal evolution of a solid phase such as the catalyst walls of each monolith channel, was considered.

WP 6 – Upscaling / Evaluation

The main objectives of WP6 included the selection of the most promising materials, their up-scaled production, the preparation of the prototypes and their performance evaluation under realistic conditions. The consortium also determined the performance of the developed prototypes according to the EU emission standards in order to justify the sustainability of the developed automotive catalysts.

1. Selection of the most promising catalysts – Up-scaling

Results from WP3, WP4 and WP5 resulted in the selection of two non-PGM catalysts for scale up in WP6. These were 2wt%Cu/CeZrO_x and 2wt%Cu/La_{0.8}FeO₃; with the CeZrO_x support being sourced from a large-scale

supplier and the lanthanum ferrite based perovskite developed within the project using flame-spray pyrolysis (FSP).

Knowledge regarding the FSP route for the formation of the perovskite catalyst was transferred from JM to TECNAN with the aim of developing this process so as to produce up-scaled batches of >100g. A 100g batch of $\text{La}_{0.8}\text{FeO}_3$ was synthesised by TECNAN and sent to JM for further development and evaluation. Previous development carried out on lab scale FSP preparation of $\text{La}_{0.8}\text{FeO}_3$ material revealed that impregnation of CuO onto its surface, resulted in an improvement in the CO/HC conversions and no loss in NO activity. Therefore, a similar approach was followed for the preparation of the $\text{La}_{0.8}\text{FeO}_3$ large batch by TECNAN.

At industrial scale, spray drying is the method of choice for loading of CuO onto supports, with the advantage of good Cu dispersions and a consistent particle size distribution. Initial studies looked at loading $\text{Cu}(\text{NO}_3)_2$ onto $\text{La}_{0.8}\text{FeO}_3$ using a lab scale spray dryer, however this study was not successful due to issues with clogging of the nozzle and product recovery. Therefore, standard wet impregnation methods were employed, comparable to that carried out on the small scale FSP batch using $\text{Cu}(\text{NO}_3)_2$ followed by calcination at 500°C. The resulting 2wt%Cu/ $\text{La}_{0.8}\text{FeO}_3$ (TECNAN) powder material was evaluated under standard JM perturbed gasoline conditions and was compared to the small scale 2wt%Cu/ $\text{La}_{0.8}\text{FeO}_3$ (JM) sample.

Characterization results revealed comparable phase purity (XRD), particle size, specific surface area and Cu dispersion (UV-Vis) between the lab scale and large scale samples. However, the sample prepared on the larger scale at TECNAN was found to have a much poorer performance with <5% conversion of NO and 20-30% conversion of CO/HC below 500°C. This catalyst therefore did not meet the NEXT-GEN-CAT requirements for $\geq 50\%$ conversion of CO/HC/NO at 500°C and highlighted reproducibility issues related to the FSP synthesis of perovskite catalysts.

The large batch (2 kg) of 2Cu/CeZrO₄ was synthesised at JM using wet impregnation of copper nitrate using a Hobart bench mixer followed by calcination at 500°C under air. The phase purity and copper dispersion were determined using XRD and UV-Vis, respectively. Results revealed good CuO dispersion, comparable to the small scale (2g) prepared samples (this was further repeated and found to be reproducible). This 2%Cu/CeZrO₄ batch was evaluated in its powder form under realistic perturbed gasoline testing conditions at JM and, similar to the lab scale catalyst, met the requirements of the NEXT-GEN-CAT with >50% CO/HC/NO conversion at <500°C. This Cu/CeZrO_x catalyst was then sent to JM for further development of a monolithic catalyst prototype.

In parallel with the up-scaling of the most promising candidate, the consortium (TECNAN and LUREDERRA) also focused on the up-scaling of SBA-15 support material considering the complexity of its wet route fabrication steps. After studying possible synthetic alternatives, an option involving inorganic raw materials was selected in order to improve the industrial production prospects towards increased availability and less demanding storage conditions. Moreover, the specific synthetic steps were assessed and the less advantageous were identified. Thus, in order to avoid such limitations, times and temperatures for the drying and calcination phases were optimized. To this end, several batches were produced at different times and temperatures and the resulting material showed interesting properties in dispersion, showing good up-scaling prospects.

Finally, the partners (TECNAN, LUREDERRA and UA) worked towards the up-scaled production of gamma- Al_2O_3 as a potential alternative to SBA-15 catalytic support. The team apart from the preparation of the support was focused on the preparation of the active phase with Cu or Cu/Ni.

2. Preparation of the monoliths

a) Monolithic Substrate Coating

The large batch of 2.0Kg of 2%w/w Cu impregnated into CeZrO₄ provided by JM was used in order for full-scale prototypes to be manufactured. The standard catalyst PGM powder wash-coat was substituted by the 2%Cu/CeZrO₄ catalyst in order for a mixed low-PGM pigment to be developed. As a result, the mixed pigment contained 45% less noble metals, replaced by Copper nanoparticles as active catalytic material.

The low-PGM pigment was used to wash-coat thirteen round ceramic monolith honeycombs (Prototype I). Furthermore, ten more honeycombs were prepared using only the 2%Cu/CeZrO₄ without any noble metals (no-PGM catalysts – Prototype II). The mantle version of all twenty three prototypes was developed by sleeving the ceramic honeycomb to the external metal canister

b) Development of Direct-Fit Prototypes for Euro applications

The stages of development of direct fit models are:

- Tooling preparation
- Jig adjustment
- Component preparation
- Cones development
- Adjustment of canning method

3. Performance evaluation of the prototypes

a) Determination of PGM substitution of Low-PGM prototype

The aim of this step was to determine the PGM substitution of NEXT-GEN-CAT prototypes compared with commercial catalysts and NEXT-GEN-CAT reference catalyst. The determination of the content of Pt, Pd, Rh, Ce, Zr and Cu took place for the following catalysts:

- Original Ford Focus 1.4lt (2000-2004)
- Low-PGM prototype
- No-PGM prototype

Thus, the accomplished PGMs substitution was 44.41% compared with original Ford Focus 1.4lt 2000-2004 catalyst.

b) Fitting of the prototype to vehicles

Two different prototypes (Low-PGM and No-PGM) were tested under real conditions. The prototypes were fitted to a car for testing under real driving conditions. The performance of the prototype was monitored and the durability of the prototype was tested using camera images presenting no mechanical (cracking) or thermal (melting) damages in normal driving conditions.

Tests were conducted to determine at which European Emission Standard the prototypes correspond to. The catalysts were proven to comply with the emission standards of Euro III and to be of equivalent quality with up-to-date commercial catalysts even if the PGMs substitution was about 45% in regards to the reference catalyst.

WP7. Recyclability studies/ LCA

The activities within WP7 were focused on the assessment of the complete life cycle of the developed TWC as well as on the definition of their end-of-life scenarios. Thus the prospects of recycling the novel spent catalysts were thoroughly examined within the project and the environmental impact of the developed

materials was determined by a Life Cycle Assessment (LCA) study. The main objective was to provide to stakeholders and policy makers a complete assessment including performance evaluation, cost, recyclability and environmental health study, in order to identify the most promising materials and to ascertain the sustainability of the novel catalysts developed within NEXT-GEN-CAT.

Recycling of PGMs from the exhausted automotive catalytic converters

Pyro-metallurgical treatment was investigated by smelting of the catalytic converters in an inert atmosphere. The theoretical study of the process revealed the optimum temperature, kind and quantity of additives (fluxes) for the effective separation of metal(s) from the formed slag. Based on the results of this study, a series of experiments was performed in a smelting furnace, at the optimized range of temperatures 1450 – 1650 °C and with the addition of the optimized amounts of SiO₂ and NaO₂ or CaO as fluxes, using copper as collector metal for PGMs recovery. According to the experimental results, under optimum conditions (temperature, retention time and amount of collector metal – Cu), the achieved PGMs recovery rates were high, reaching 90% for Pt and about 85% for Pd and Rh. The Pt recovery was governed by the mechanism of setting through the slag, while in the case of Pd and Rh recovery, the mechanisms of metal particles setting and wetting operated as well, but setting seemed to be more important. The most important advantage of the pyrometallurgical process for PGMs recovery is the fact that it is a well-established process (primary production of copper) that can be improved to achieve 100% of PGMs recovery. Its main drawback is related to the loss of all other valuable metals in the slag.

The hydrometallurgical treatment of the exhausted automotive catalytic converters was investigated in the system HCl / H₂O₂; where H₂O₂ acts as an oxidizing agent transferring PGMs from their metallic form to the ionic, while HCl acts as a chelating agent for metal ions, keeping them in dissolution. The experimental results of PGMs leaching revealed that, under optimum conditions (retention time, temperature, solid to liquid ratio, stirring rate, concentration of HCl and HCl to H₂O₂ ratio), the studied system was effective for the Pt and Pd recovery, unlike Rh. The process is fast and seems to be completed within the first hour, while the most important parameters that affect PGMS recovery are the temperature and HCl concentration. At optimal process conditions, the recoveries of Pt, Pd and Rh were equal to 99%, 87% and 58%, respectively. Concerning the other valuable metals contained in the exhausted automotive catalytic converters, leaching process achieved 70% of La recovery, while recovery of Ti was low, ranging from 5 – 12%. Zr however was not leached.

Therefore, both investigated processes reach high PGMs recovery rates; however the pyrometallurgical treatment is more advantageous, as it achieves high recovery for all PGMs and is based on a well-established metallurgical process.

Recycling of transition metals (Cu and Ni) from the exhausted automotive catalytic converters

Recycling of transition metals (Cu and Ni) was studied via hydrometallurgical processing of metals leaching. To this end, the effect of different leaching agents (acidic: aqueous solutions of hydrochloric acid, sulphuric acid, nitric acid and oxalic acid and basic: the aqueous solution of ammonia / ammonium sulphate) on the recovery of Cu and Ni was investigated. Moreover, basic process parameters were investigated including temperature, stirring rate, retention time and solid to liquid ratio (S/L). According to the experimental results, under optimum conditions, 100% leaching of Cu was achieved, while Ni recovery reached 80%. From the resulted leachates, the recovery of Cu and Ni in the form of salts or pure metals via precipitation and electrolysis methods was also studied theoretically and experimentally. The experimental results showed that

both methods were effective for the recovery of transition metals from exhausted automotive catalytic converters.

Regeneration of deactivated catalytic converters

The regeneration of the deactivated **Low PGMs** prototype catalytic converters was investigated, following thermal treatment in a tube furnace with a stream of oxygen gas at the temperature of 600 °C for 6 h. The whole investigation included the following steps: (i) SEM/EDS study / activity determination of the fresh catalyst and; (ii) SEM/EDS study / activity determination of the deactivated catalyst; (iii) regeneration with O₂ and (iv) SEM/EDS study / activity determination of the regenerated catalyst.

According to the results of the SEM/EDS studies, the main pollutants leading to catalyst deactivation are related to carbon, namely hydrocarbons (HC) and carbon monoxide (CO). Sulphate and phosphorous were also identified on the wash-coat particles of the deactivated catalyst. Deactivated catalyst exhibited lower activity compared to the fresh one, while after regeneration, SEM and EDS studies revealed the elimination of pollutants (C, S and P) from the wash-coat. Regeneration allowed the catalyst to regain its activity in HC, CO and NO_x conversion rates, as after regeneration, the catalyst reached almost 100% of its activity before deactivation.

Life Cycle analysis

The objective was to characterize the environmental impact due to the manufacture of a conventional three-way catalyst, including the washcoat process and more importantly, to compare the reference data with the novel designed and produced nanocatalysts. As studied in the beginning of the project, the total impact of a conventional catalyst is around 93.5 Eco-points. These traditional three-way catalysts use a variety of metals to reduce emissions of CO, NO_x and hydrocarbons with their most common components being PGMs (Platinum Group Metals), with a large environmental impact related to their extraction. Their impact value reaches 92.5 Eco-points, with 2.95 grams of PGMs in 554.02 grams of total washcoat slurry.

During the entire project, novel catalytic systems based on nanotechnology were developed (WP2) and upscaled (WP6) to final catalytic converters. For the LCA study carried out by LUR it was assumed that the novel catalysts had the same weight compared to the traditional ones and that the active compound was 3g. In all cases studied, the PGMs loading was 45% of the amount used in commercial TWC.

The results obtained in the three first cases were totally favourable as the environmental impact of selected new wash-coats is negligible compared with a traditional ones. The best environmental impact was obtained for the SBA-15 sample doped with Cu, synthesised by NCSR. The sample reached as low as 0.13 Eco-points, with the main contributor being fossil fuels consumption. The other two samples, mixed oxide of Ce/Zr impregnated with copper (JM) and the copper doped La_{0.8}FeOX up-scaled by TECNAN and impregnated by JM represent 0.25 and 0.52 Eco-points respectively.

In all three cases the environmental impact increases clearly because of the PGMs addition. The 34 Eco-points are mainly attributed to the "*Respiratory Inorganics*" category, which largely affects human health. Based on the analysis, it can be concluded that the new nanostructured catalysts exhibit 711 times lower environmental impact compared with the conventional three way catalytic converter, while addition of 55% PGMs, increased the Eco-Points. However, even that case, the overall environmental impact is almost the one third of the conventional TWC.

WP8. Innovation-related activities

The main objective of WP8 was to increase the visibility and impact of the NEXT-GEN-CAT on the research community at both European and International level. The main pillar of the NEXT-GEN-CATs dissemination activities was the project website www.nextgencat.eu, which was based on partners' contributions. The material presented, was updated constantly during the project and in its public section it contained dissemination material including articles, press releases, brochures, presentations etc.

Other key activities under this WP were the:

- Dissemination of the scientific and technical results. The main target was the participation of the consortium partners in high visibility conferences, workshops, science fairs and events with the industry. Furthermore the partners disseminated the foreground by publishing the obtained results to scientific journals.
- Technology transfer to the industry by establishing synergies with the industrial and academic communities
- The participation of the NEXT-GEN-CAT members to events that could increase the public awareness and create synergies with society (Researcher Night events, Gallileo Innovators Festival 2013, North-West European days of young researchers etc.).
- Networking activities by participating in relevant bodies, like in CRM-Innonet, CRM cluster and Catalysis Cluster
- Training activities within the consortium in order to strengthen the dissemination objective

In accordance with the DoW the final workshop of NEXT-GEN-CAT project was aiming to disseminate the results of NEXT-GEN-CAT to a wider community. The event was open to participants from both industry and academia and included presentations from the participant members as well as from invited speakers specialized in catalysis and nanotechnology topics. Correspondingly, the one-day workshop included key note lectures, oral presentations, rapid presentation and an interactive panel discussion session. The **1st Workshop on Critical materials in Catalysis: the case of automotive catalysis** was held on 29th January 2016 at the University of Lille (P. Glorieux Auditorium) and attracted more than 50 participants.

- In order to support the exploitation of the obtained results, an Exploitation Strategy Seminar (ESS) was held at Antwerp (25th January 2013) together with the 12th month meeting, with G. Hiemstra from Van der Meer & van Tilburg B.V and the collaboration and support of NEXT-GEN-CAT partners.
- Based on partners' feedback the Contribution Benefit Matrix table was prepared. This document was used as a management tool throughout the project. Furthermore, the consortium identified the potential exploitable results while the technical risks and the interventions were discussed thoroughly. Additionally, a Plan for Using and Disseminating Foreground was prepared.
- Finally, for the training activities, the main objective was to promote sustainability and knowledge transfer in the general field of Nano-materials and more specifically in the automotive nanostructured catalysts. The specific targets of the training activities, divided in internal (within the consortium) and external (outside the consortium) were:
 - the transfer of knowledge within the participants including students, researchers and industrial staff.
 - the staff training in multidisciplinary areas including materials' preparation and characterisation, performance evaluation and modelling as well as materials' up-scaling and prototyping
 - the spreading of knowledge from both the academic and industrial experts within NEXT-GEN-CAT to young scientists and industrial staff outside the consortium, promoting S&T cohesion within the European Research Area and so increase skills across Europe

Potential impact of the obtained results

NEXT-GEN-CAT proposed an integrated approach on the preparation of innovative, low cost and highly effective nanostructured automotive monolithic catalysts based on the partial replacement of noble metals by transition metal nanoparticles (TMN). The proposal targeted on the development of a novel method for commercial (large-scale) preparation of nanostructured materials in the monolithic form, providing not only the research platform for their development but also the necessary engineering tools for their effective adaptation in the automotive fields. The aim was to combine molecular engineering and process simulation to develop novel eco-friendly nano-structured catalysts based on transition metals (Cu, Co, Cd, Pb, Zn, Fe etc.) capable of exhibiting increased catalytic performance, even at low temperatures (200-250°C). Taking into account that the auto catalyst industry uses extremely large quantities of precious metal- 60% of total supply of Pt and 65% of Pd – the impact of replacing PGMs is of tremendous importance. Other key targets of the current proposal include the: i) Excellent dispersion of the metal nanoparticles, ii) Controllable size, iii) Thermal stability (avoiding aggregation at high temperatures), iv) Improved durability, v) Recyclability / Recovery of transition metals, vi) Low health and environmental impact.

The main achievement of the project was the upscaling of two most promising catalysts and the development of two prototypes, as after treatment systems. Regarding the upscaling, data obtained from WP3, WP4 and WP5 resulted in the selection of two non-PGM catalysts for scale up in WP6. These were 2wt%Cu/CeZrO_x and 2wt%Cu/La_{0.8}FeO₃; with the CeZrO_x support being sourced from a large-scale supplier and the lanthanum ferrite based perovskites developed within the program using flame-spray pyrolysis (FSP).

The large batch (2 kg) of Cu/CeZrO₄ was synthesised at JM by wet impregnation of copper nitrate using a Hobart bench mixer followed by calcination in air at 500°C. The phase purity and copper dispersion were characterized using XRD and UV-Vis, respectively. Results revealed good dispersion of CuO, comparable to the small scale (2g) prepared samples (this was further repeated and found to be reproducible).

At the industrial scale, spray drying is the method of choice for loading of CuO onto supports, with the advantage of good Cu dispersions and a consistent particle size distribution. Initial studies looked at loading Cu(NO₃)₂ onto La_{0.8}FeO₃ using a lab scale spray dryer, however this study was not successful and resulted in issues with clogging of the nozzle and product recovery. Therefore, the partners had to conform to standard wet impregnation methods, comparable to the ones carried out on the small scale FSP batch using Cu(NO₃)₂ followed by calcination at 500°C. The resulting 2wt%Cu/La_{0.8}FeO₃ (TECNAN) powder material was evaluated under standard JM perturbed gasoline conditions and compared to the small scale 2wt%Cu/La_{0.8}FeO₃ (JM) sample. Characterization results revealed comparable phase purity (XRD), particle size, specific surface area and Cu dispersion (UV-Vis) between the lab scale and large scale samples. However, the sample prepared on the larger scale at TECNAN was found to have a much poorer performance with <5% conversion of NO and 20-30% conversion of CO/HC below 500°C. For this reason, it was decided that this sample would not be incorporated into a monolith.

The next stage of the prototype development was the preparation of the coating pigment for the ceramic honeycomb (monolith) wash-coating. The 2%Cu/CeZrO₄ catalyst substituted by 45% the standard catalyst powder used to wash-coat the prototypes. As a result, the mixed pigment contains 45% less noble metals which have been replaced with Copper nanoparticles, as active catalytic material. The low-PGM pigment, as used to wash-coat eight round ceramic monolith honeycombs. For comparison purposes, four more honeycombs were prepared with just 2%Cu/CeZrO₄, without any noble metals (no-PGM catalysts) and four more with the standard PGM containing slurry (only-PGM catalyst).

The mantle versions of all prototypes were developed by sleeving the ceramic honeycomb to the external metal canister. Four different direct-fit prototypes were manufactured. Furthermore, small monoliths, for all kinds of the prototypes (Low-PGM, No-PGM and Only-PGM), were developed and sent to the corresponding partners to perform laboratory emission (WP5) and recycling/regeneration studies (WP7).

The fitted prototypes were evaluated under real driving conditions. The emission results in all cases were well below European Emissions standards (Euro III). However the No-PGM prototype exhibited increased pollutants emissions. The prototype with 45% less PGMs (Low-PGM) was also fitted to the engine without any problems (cracking or thermal shock effects). This prototype was successfully evaluated according to Euro III standard.

The development of increased efficiency prototypes containing 45% less PGMs is of significant importance. Concerning the **environmental impact**, there is a continuous focus on controlling the emissions of pollutants from engines around the world as combustion of fossil fuels is by far the dominant source of CO and NO_x emissions. The emissions are not dependent solely on the quality of the fuel but also on the air- fuel mix ratio. For example, high temperatures and oxygen-rich conditions generally favour NO_x formation in combustion. NO_x contributes to acid deposition and eutrophication which in turn can lead to potential changes occurring in soil and water quality. The subsequent effect of acid deposition can be significant, including adverse effects on aquatic ecosystems in rivers and lakes and damage to forests, crops and other vegetation. Eutrophication can lead to severe reductions in water quality with subsequent impacts including decreased biodiversity, changes in species composition and dominance, and toxicity effects. In many cases, the deposition of acidifying and eutrophying substances still exceeds the critical loads of the ecosystems.

Furthermore, NO₂ is associated with adverse effects on human health, as at high concentrations it can cause inflammation of the airways. NO₂ also contributes to the formation of secondary particulate aerosols and tropospheric ozone (O₃) in the atmosphere - both are important air pollutants due to their adverse impacts on human health. NO_x is therefore linked both directly and indirectly to effects on human health.

Significant reductions in CO and NO_x emissions have occurred in the 'road transport' sector since the early 1990s, with an overall 36 % decline in emissions between 1990 and 2008. This has been achieved despite the general increase in activity within this sector over this period. However the scientific efforts should be continued to meet the requirements of the tighter Euro 6 limits.

The synthesis of nanostructured materials based on transition metals and their functionalization in large-scale to be used as automotive catalysts was realized within NEXT-GEN-CAT through the low-cost novel techniques that were developed by the consortium. These techniques led to excellent dispersion of metal nanoparticles into the catalytic substrates offering high catalytic efficiency, low cost and environmental compatibility.

Current trends in autocatalysts involve the reduction of precious metal loading. Initial studies in the field, revealed that precious metal loadings on automobile catalysts can be reduced by 20% over the next few years, largely through the use of nanomaterials. This would result in a production savings for the auto industry of €230M per year. According to similar studies, 50% reduction of about 50% in PMG used in current catalysts will account for an annual saving of as much as €4 to €7 billion.

On the other hand, if automobile catalysts could be designed so that no precious metals were required, this savings could increase to €1,100M per year. Furthermore, **since the cost of Pt is at about 100-1000 times higher than transition metals (100 times for Co, 160 times for Ni, 450 times for Cu and 1000 times for Zn) the estimated reduction in automotive catalysts reaches about 40-50%**. In addition, the preparation of effective catalysts using nanotechnology tools **is expected to reduce the cost more than 10-15% offering also increased**

catalytic conversion even at low temperatures (200-250°C). This will open the way to an efficient adaptation of nanotechnology-based automotive catalysts and will facilitate the upscaling of the proposed materials via the expertise of the industrial partners for viable applications in the automotive sector.

There are also **important societal implications** beyond the NEXT-GEN-CAT project's research and technical objectives. The proposed innovative materials and processes will contribute to the improvement of the environment and the quality of life. There is a range of drivers for environmentally sustainable manufacturing, which may affect any stage of the process, from cutting cost by saving critical materials (especially Pt and Pd) and energy to unnecessary short material life cycles and regulations set by authorities. Since the PGMs are quite limited on earth, their effective replacement with low cost transition metals in automotive catalysts, will secure the undisturbed supply of the European industry with critical resources, eliminating problems that can be faced in the future due to overexploitation or trade and political restrictions. The availability of copper, cobalt, nickel, iron and zinc in Europe even at small quantities as well as their worldwide abundance, enable the secure flow of raw materials in our continent, strengthening the leadership of European companies in the automotive sector.

Concerning the materials' synthesis, preparation of efficient, transition metal based, automotive catalysts was of primary importance. The consortium applied several nanotechnology strategies including grafting, assisted and controlled impregnation, co-condensation, direct functionalisation, sol-gel/bio-silicification, modified polyol, wet chemistry, citrate methodology and flame spray pyrolysis for the preparation of active catalysts. Some of these methodologies were also subject to further optimisation. Overall more than 300 samples for the various categories of the materials namely silicas, silicon carbides, perovskites and doped perovskites were prepared and evaluated, using the protocols developed within the project. The majority of the samples exhibited acceptable CO and HC oxidation, while only 10 samples reached the target for NO conversion. From the scientific point of view, the successful preparation of such materials contributed significantly to the research efforts towards PGMs replacement by transition metals.

The preparation of nanomaterials with desired properties will contribute to the extensive research involving nanotechnology being performed by almost all leading industrial companies in a wide range of applications such as electronics, medical, aerospace, defence, automotive, energy, construction, etc. It is projected that nanotechnology will become by 2016 "a trillion dollar industry", with Nanomaterials market being its largest segment (€310 billion annually). A significant part of the nanomaterials' market is related to catalysts for energy and environment. Thus, the global market for catalysts was worth about €15.1 billion in 2009 and it is expected to reach nearly €22.5 billion by 2015. The greatest portion of this market concerns the environmental catalysts, with projected growth from €12.3 billion in 2010 to €16.5 billion in 2015. The three main segments of the environmental catalyst market are catalysts used in vehicles and in stationary air pollution sources as well as in municipal waste treatment systems.

Important results were also obtained by the characterisation of the materials. The applied conventional and operando or *in-situ* techniques shed light on the mechanisms involved during the preparation of the materials, at the nanoscale, and enabled their optimisation. Additionally, the determination of specific properties, including metal dispersion, redox properties, oxygen storage capacity etc., revealed the developed materials' potential, as to their application in other fields of catalysis such as biomass conversion, water-gas shift reaction, conversion of carbon dioxide to fine chemicals etc.

Another significant aspect of NEXT-GEN-CAT was the multiscale modeling. The largest barrier to rational design and controlled synthesis of nanomaterials with predefined properties is the lack of fundamental understanding of thermodynamic and kinetic processes at the nanoscale. Today, the interactions at nano- scale

are not well understood nor do we have the ability to bridge length scales from nano to micro to macro. This lack of basic scientific knowledge regarding the physics and chemistry of the nanoscale significantly limits the ability to predict a priori structure-property-processing relationships. The consortium developed theoretical models for the simulation of the surface properties of the nanostructured catalyst and the prediction of their final catalytic properties. The obtained results were of high scientific importance and lead to the preparation of the most efficient catalysts.

Through the recyclability studies, pyrometallurgical treatment of the spent catalytic converters that contain **precious metals** proved more effective for their recovery compared to the hydrometallurgical one. The only disadvantage of the pyrometallurgical processing is the loss of other valuable metals of catalytic converters in the resulting slag. However, as discussed previously in this report, the hydrometallurgical treatment of the spent catalytic converters does not achieve to recover the other valuable metals contained in the catalytic converters either, as their leachability, with the exception of La, was very low (Ti) or negligible (Zr). On the other hand **transition metals** recovery from the spent catalytic converters is efficient with the conventional hydrometallurgical processing of leaching metals. The metals are recovered from the resulted leachates by precipitation (as oxides), or as by electrolysis (pure metals).

Furthermore, regeneration studies (using SEM/EDS) revealed that the main pollutants causing catalyst deactivation are related to carbon (e.g. hydrocarbons and carbon monoxide). Sulphate and phosphorous were also identified on the wash-coat particles of the deactivated catalyst. Deactivated catalyst presented lower activity compared to the fresh one. After regeneration, SEM and EDS studies revealed the elimination of pollutants (C, S and P) from the wash-coat, allowing the catalyst to regain almost 100% of its HC, CO and NO_x conversion rates.

The excellent S&T results obtained from pollutant degradation and environmental analysis (LCA), combined with the proven production scalability, reinforce the success of the project towards the design and manufacture of novel catalysts. In fact, despite the complex compositions studied, there are remarkable achievements in the formulation of both support and active species for nanostructured catalysts. Moreover, it is worth mentioning that the preliminary estimated prices for the upscaled novel catalytic compounds are very reasonable considering current market competition, mainly thanks to the advantages of FSP technology against other alternatives. For Ce/Zr nanoparticles, the commercial calculated prices are in the range of 250€/Kg, and taking into account its content in a relatively critical material such as Ce, its price is very competitive. Indeed, although for other technologies like gas phase synthesis the cost is lower, only few oxides can be produced without the capability of production of complex species like the ones designed within the present project. Besides, traditional catalysts contain large amounts of scarce and expensive materials like PGMs, so the materials proposed by the NEXT-GEN-CAT project, offer a very interesting alternative for catalytic converter manufacturers. In this sense, good prospects are established for nanomaterial producers like TECNAN. Additionally, regarding the potential socioeconomic impact, conservative market estimates for metal oxide nanoparticles production by 2020 rise to 1663168 tons. Hence, exploitation of the NEXT-GEN-CAT project results will allow direct addressing of this market segment. NEXT-GEN-CAT's success is a step towards reinforcing of the European nanotechnology-based products industry and commercialisation of new efficient and competitive applications. On the other hand, regarding the impact on the environment, Flame Spray Pyrolysis technology as well as the specific wet route selected for SBA-15, have been assessed and resulted in a considerably lower environmental impact than traditional catalysts preparation processes.

Summarising, the main exploitable result was the development of the prototypes as proof of concept. The evaluation results exhibited the material's high potential for use in the automotive after treatment sector.

However due to the harsh conditions and the enforcement of stricter regulations, further validation of both the material and the prototypes, is needed before commercialization.

Dissemination

The dissemination of the obtained foreground was a key point for NEXT-GEN-CAT. The communication and dissemination strategy was necessary to maximize the benefits of the projects' outcomes.

The principal objectives for dissemination in the NEXT-GEN-CAT were:

- to widespread the project results to the European and International scientific and research communities
- to inform the wider audiences of interested parties (thematic stakeholders) about the project, namely about the research design and its scope, as well as on the project results and outcomes
- to influence future industry, in particular automotive industry, companies specialized in catalysis and materials science
- To open the debate between academic and industrial sectors about nanotechnology in technological and research issues as well as on societal impact of novel technologies.

The dissemination strategy included both the spreading of results in the international level as well as targeted at a local level. The plan used mainly the conventional dissemination tools including printed material, participation in and organization of workshops, publications in scientific journals etc. Furthermore, electronic communication tools together with the project's website were used for the diffusion of the scientific and technological outcomes mainly to wider audiences and to general public.

The key target groups for dissemination, outreach and training were:

- Scientific communities
- Industry
- Policy makers
- General public

The main pillar of the dissemination activities of NEXT-GEN-CAT was the project website www.nextgencat.eu, which was based on the partners' contribution. The presented material was updated constantly during the implementation of the project and in its public section it contained dissemination material including articles, press releases, brochures, presentations etc.

The participation of the consortium partners to top class conferences, workshops, science fairs and events with the industry was another very useful dissemination tool. The partners have contributed to more than 30 scientific conferences/events. The project participants have delivered 12 lectures and have presented more than 30 posters with the NEXT-GEN-CAT results.

In addition, NEXT-GEN-CAT members participated to events that could increase public awareness and create synergies with society including Researcher Night events, Gallileo Innovators Festival 2013, North-West European days of young researchers etc.

Furthermore, the final workshop of NEXT-GEN-CAT project was organized, aiming to disseminate NEXT-GEN-CATs results to a wider community. The event was opened to participants from both the industry and academia and included presentations from the participant members, as well as from invited speakers specialised in catalysis and nanotechnology topics. The organising committee in order to maximise the impact of the event selected 3 well-known scientists from the automotive catalysis sector as invited lecturers, namely:

- Dr. Santhosh Kumar Matam, EMPA, Switzerland
- Prof. A. Trovarelli, Univ. Udine, Italy

- Dr. Arnaud Frobert, IFP Energies Nouvelles, France,

Correspondingly, the one-day workshop included key note lectures, oral presentations, radio presentation and an interactive panel discussion session. The 1st Workshop on Critical materials in Catalysis: the case of automotive catalysis, was held on 29th January 2016 at the University of Lille (P. Glorieux Auditorium) and attracted more than 50 participants.

Furthermore the partners disseminated the foreground by publishing the obtained results to scientific journals. The consortium has published a relatively small number of publications (10). However 4 more manuscripts have been submitted and they are under review. All publications have been submitted by academic partners. In several publications, more than one partner has contributed, revealing the close interaction and collaboration between partners within the project. Additionally the managing team has contacted the editorial boards of several journals in order to publish a special issue based on the results obtained by the project. The Current Nanoscience journal, (<http://benthamscience.com/journals/current-nanoscience/>) agreed to publish a thematic issue on NEXT-GEN-CAT. The consortium is currently working on the preparation of this special issue, which will contain 6 manuscripts based on NEXT-GEN-CAT results.

Regarding training activities within the project, 5 PhD candidates and 12 Master Thesis students were trained to the various disciplines of NEXT-GEN-CAT. Based on the initial training plan, short term exchanges of young PhD/Master students and post doctorate researchers were implemented. The secondees were trained in complementarity to their original scientific fields, thus enhancing the interdisciplinary nature of the project. Furthermore, more than 20 post-doctoral fellows worked for the project.

Exploitation

In order to support the exploitation of the obtained results, an Exploitation Strategy Seminar (ESS) was held in Antwerp (25th January 2013) together with the 12th month meeting. The seminar was contacted by G. Hiemstra from Van der Meer & van Tilburg B.V with the collaboration and support of NEXT-GEN-CAT partners. Based on the partners' feedback, the Contribution Benefit matrix table was prepared. This document was used as a management tool throughout the project. Furthermore, the consortium identified the potential exploitable results while the technical risks and necessary interventions were discussed thoroughly. Additionally, a Plan for Using and Disseminating Foreground was prepared.

The consortium had assigned Mr. Iakovos Yakoumis (MONOLITHOS) as the Exploitation Manager (EM) of NEXT-GEN-CAT. The Exploitation Manager was responsible for:

- Updating the Plan on the Use and Dissemination of Foreground (PUDF) intellectual property, developed during the project as contractual requirement, and organizing any action necessary to protect the generated Intellectual Property Rights (IPR).
- Formulating a strategy for exploitation and dissemination in close co-operation with the Consortium, in order to identify exploitation opportunities, business scenarios and development activities.

Therefore EM designed an exploitation strategy aiming at:

- Better Understanding of the state-of-the-art commercial catalytic converters and the state-of-the-art commercial catalytic converters recycling processes
- Contact European buyers of automotive catalytic converters (car manufacturers, exhaust systems manufacturers, catalytic converter manufacturers) in order to determine the potential market for the NEXT-GEN-CAT catalyst
- Contact European Recycling Industries to locate possible interested companies for the recycling process of NEXT-GEN-CAT

- Formulate a business strategy for the commercialization of the novel catalyst (including funding possibilities, clients, business plan, etc.) and the recycling process.

Some of the EM actions included:

1. Contact with a main after sales catalyst supplier in the Czech Republic (March 2012). The discussion focused on the cost of the Precious Metals as a percentage of the total cost of the manufacturing of catalytic converters.
2. Visit Automechanica Fair in Frankfurt (September 2012). Automechanica is the World's Leading Trade Fair for the Automotive Industry (<http://automechanika.messefrankfurt.com/frankfurt/en/besucher/messeprofil.html>). During the Fair, the EM had the chance to contact and discuss with some of the largest companies in Exhaust Manufacturing Systems and Catalytic Converters. The aim of the visit was to locate potential interested companies for the NEXT-GEN-CAT catalyst.
3. Contact with PGMs refiner in Frankfurt (September 2012) and Umicore Refinery in Antwerp (January 2013) in order to investigate the commercial PGM refining process problems and potential solutions.

The aforementioned visits provided the EM a very valuable business perspective for the problems and the costs of both processes of interest to NEXT-GEN-CAT: development and manufacturing of the novel catalyst and recycling of PGMs and transition metals included in the novel catalyst.

Several visits took place to companies, potentially interested of the novel products/processes of the project:

1. Car manufacturers:
 - FIAT Chrysler Group (Torino, Italy)
 - Ford Otosan (Istanbul, Turkey)
 - Toyota Motor Company, Europe (Brussels, Belgium)
2. Exhaust systems and catalysts manufacturers
 - TENNECO/Walker Automotive (Spain)
 - AS Catalysts sl. (Spain)
 - Cats and Pipes (UK)
 - AWG Catalysts (Poland)
 - European Exhausts and Catalysts (UK)
 - Agar Oto Egzoz (Turkey)
 - Soylu Exhaust and Emission Control Systems (Turkey)
 - Hobi Exhaust Ltd. (Turkey)
 - Magnaflow Performance Exhaust (Italy)
3. PGMs and Automotive Catalytic Converters Recyclers
 - SAR Metals (UK)
 - JMC Recycling Machines (UK)
 - BASF Recycling (UK)
 - Emak Refining and Recycling (Turkey)

The main outcome of those meetings was the identification of the tests that the new catalyst/process should go through in order for the companies, especially the key players (FIAT/Chrysler, Ford, TOYOTA, TENNECO, BASF, etc.) to be interested in exploiting.