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Environmental catalysis: trends and outlook

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Abstract

Environmental catalysis has continuously grown in importance over the last 2 decades not only in terms of the worldwide catalyst market, but also as a driver of advances in the whole area of catalysis. The development of innovative "environmental" catalysts is also the crucial factor towards the objective of developing a new sustainable industrial chemistry. In the last decade, considerable expansion of the traditional area of environmental catalysis (mainly NO_x removal from stationary and mobile sources, and VOC conversion) has also occurred. New areas include: (i) catalytic technologies for liquid or solid waste reduction or purification; (ii) use of catalysts in energy-efficient catalytic technologies and processes; (iii) reduction of the environmental impact in the use or disposal of catalysts; (iv) new eco-compatible refinery, chemical or non-chemical catalytic processes; (v) catalysis for greenhouse gas control; (vi) use of catalysts for user-friendly technologies and reduction of indoor pollution; (vii) catalytic processes for sustainable chemistry; (viii) reduction of the environmental impact of transport. Therefore, a significant change has occurred in the last decade in the areas of interest regarding environmental catalysts and in the modality of approaching the research. This review, based on but not limited to the workshop "Environmental Catalysis: A Step Forward" (Maiori, Italy, May 2001), introduces the proceedings of this workshop reported in this issue of *Catalysis Today* and has the objective of providing an overview to the topic and setting the basis for a step forward in environmental catalysis research.

Keywords: NO_x; Volatile organic compound; Catalysis

1. Introduction

Catalysis is a key technology to provide realistic solutions to many environmental issues, but is also an important marketing opportunity. Currently the world market for catalysts is about 9 billion US $, about a third of which involves environmental catalysis. Fig. 1 shows the expectations for growth in the worldwide catalyst market through the year 2005, by general industry segment. Expectations for growth in the environmental catalysis area are indeed high. The US NIST "White Paper on Catalysis and Biocatalysis" of 1999 indicates environmental catalysis as being among the top five areas of US industry which combine technology challenges and economic benefits. In addition, there are a number of critical emerging scientific platforms in the area of environmental catalysis which are expected to have a high inter-industry impact.

Environmental catalysis refers to catalytic technologies for reducing emissions of environmentally unacceptable compounds. Problems addressed in regard to these catalytic cleanup technologies are mobile emission control, NO_x removal from stationary sources, sulfur compounds and VOC (volatile organic compound) conversion, liquid and solid waste treatment (polymers and other solid waste), and greenhouse

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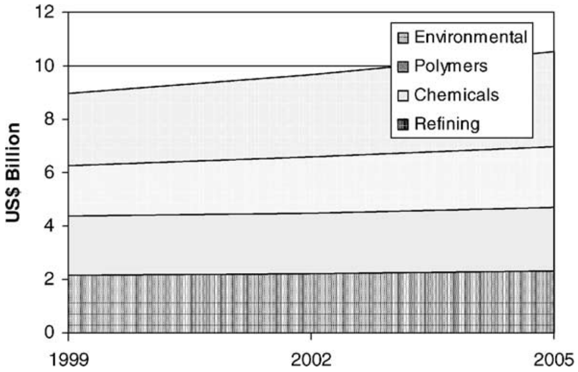


Fig. 1. Worldwide catalyst market expectations by general industry segment.

gas abatement or conversion. Environmental catalysis also encompasses the application of catalysis for new eco-compatible refinery, chemical or non-chemical catalytic processes, catalytic technologies for minimization of waste, and new catalytic routes to valuable products without the formation of undesirable pollutants. Energy-efficient catalytic technologies and processes (catalytic combustion, catalysis in fuel cells, catalytic devices for using renewable energy sources like solar energy or biomass), catalysis in the reduction of the environmental impact of transport (not only use of catalysts in emissions control, but also inside the engine to improve combustion, on the radiator to abate ozone, etc.), and catalysis use in refineries to produce new fuels (produce ultra-low sulfur fuels, reformulate fuel, upgrading heavy or not used fractions to produce clean fuels, etc.) also fall within the definition of environmental catalysts. Other areas are the use of catalysts for user-friendly technologies (e.g., to develop intelligent or self-cleaning materials) and the reduction of indoor pollution (conversion of ozone, formaldehyde and other organic indoor pollutants, but also photocatalytic antibacterial air purification), and catalytic technologies for the decontamination of polluted sites (soil and water remediation, including areas contaminated by military actions). Finally, the reduction of the environmental impact in the use or disposal of catalysts must also be cited as part of the objectives of environmental catalysis.

Historically, the interest of researchers working in the area of environmental catalysis was initially focused mainly on NO_x control (mobile and stationary sources), and sulfur and VOC abatement, as indicated by the prevailing contributions in this area at the first meetings [1–3]. Scientific interest progressively then moved from the cleanup approach to the other cited subjects. However, recently new problems and questions have renewed research activity in the area of catalytic cleanup technologies. Three main driving forces may be cited: (i) the need to expand catalytic technologies from gaseous emissions to the treatment of liquid emissions and solid waste, (ii) the need for new post-treatment devices for mobile sources and (iii) the necessity of reconsidering post-treatment technologies in the perspective of process or systems integration.

Therefore, a significant change occurred in the last decade in the area of interest of environmental catalysts and in the modality of approaching the research. This implies the necessity for re-examination of the whole area of environmental catalysis in order to determine future directions of research and identify the most critical issues to address, but also the need for fundamental and applied research.

These questions were the characterizing aspect of the workshop "*Environmental Catalysis: A Step Forward*" held in Maiori (Italy) on 2–5 May, 2001. This issue of *Catalysis Today* collects the oral presentations given at the workshop. Very interesting contributions were also reported in the poster sessions, but due to space limitations they have not been included in this issue; their abstracts can be found in the book of abstracts available on line at the following address: http://www.sci-gic.org/activ.html.

The aim of this introductory chapter is to provide an overview to the topic in order to put it in a more general perspective and thus contribute in defining how to make a step forward in the research on environmental catalysis. This review is based on but not limited to the contributions (oral and posters) given in the cited workshop.

2. Features of environmental catalysis

Some specific aspects differentiate environmental catalysis from other fields of catalysis [4]:

(i) Unlike catalysis for chemical production and refineries, it is often necessary in environmental catalysis to develop technology able to efficiently operate at the conditions defined by upstream units (i.e., the feed and reaction conditions cannot be adapted to maximize conversion or selectivity as in chemical catalytic processes).

(ii) Environmental catalysis finds application not only in refinery and chemical processes, but also in several applications for the treatment of emissions in other types of production (electronic, agro/food production, pulp and paper, leather and tanning, metal finishing companies, etc.), household or indoor applications (self-cleaning catalytic ovens, domestic burners, water purifiers, etc.), and in auto, ship and flight emissions control. Environmental catalysis spreads the concept of catalysis from the chemistry precincts to the general area of industrial production and daily life. Therefore, it allows defining catalysis as a central technology for improving the quality of life and a sustainable future.

(iii) Environmental catalysts often operate in more extreme reaction conditions than catalysts for chemical production or refineries (very low or very high temperatures, in the presence of non-removable poisons, with very high space velocities, with ultra-low concentrations, etc.) and sometimes also should operate efficiently with a range of different feeds or in the presence of fast changes in feed composition.

Environmental catalysis thus addresses different problems from those characteristics of heterogeneous catalysis, although it shares a common background of knowledge. As a consequence, new types of approaches are being investigated in the field of environmental catalysis to solve its specific problems. This area is thus characterized by a considerable degree of innovation in terms of types of catalytic materials and technologies. Several new findings may later also find application in other fields of catalysis and thus environmental catalysis is a stimulus for research in all the areas of catalysis and industry.

3. “Catalysis everywhere”

Catalysis has been traditionally associated with chemical and refinery production. Catalytic converters for treatment of car emissions constituted the first massive use of catalysis outside chemical and refinery production, greatly contributing in the spread of knowledge on the benefits of catalysis for improving the quality of the environment and life. In recent years, catalytic environmental technologies have been rapidly expanded to several new areas offering new opportunities: (i) for a range of industrial sectors traditionally far from the use of catalysis and (ii) in user-friendly devices to improve the quality of life and the indoor environment.

The plenary lecture of the workshop given by P. Landri and M. Berndt (Engelhard) focused on the market needs and trends for non-standard environmental catalysis and on the fundamental scientific and technical questions opened by these kinds of applications. Non-standard applications are a fast increasing market with respect to the consolidated traditional areas (automotive emissions—cars, motorcycles, buses, trucks and service vehicles and industrial stationary emissions—co-generation and gas turbine-based power generation facilities, biomass fired boilers, process industries, soil remediation applications).

Non-standard applications often require a more flexible and customized approach, and low per unit costs. Interesting examples are: (i) thin-walled stainless steel plates coated with a catalytic layer to be applied as hydrogen recombiners (to avoid the possibility that large amounts hydrogen be released as fall-out inside the reactor containment, with explosion risks; the same technology can be applied to rechargeable batteries, toothbrushes and other household products, and to safety devices in chemical reactors); (ii) ceramic honeycomb or metal ring-nets coated with catalysts to be applied in self-cleaning household ovens (to eliminate grease drops, CO and noxious fumes during pyrolytic processes; a similar technology can be applied to “rapid cook” residential ovens, restaurant chain driven charbroilers, air quality improvement in other commercial applications—bakery, fishery, etc.), and (iii) ozone smog reducers (radiators coated with catalysts to convert ozone to O_2; the same or similar technology is applied to filters or forced-air systems, air conditioning ducts of an aircraft, specific equipment to be added to air conditioning condensers and heat pumps, ozone converters in jet aircrafts, in office equipment, etc.).

The cited examples show some interesting concepts which are worth emphasizing:

- Structured catalysts, in the form of ceramic or metallic monoliths (often with a customized design) are necessary in these non-standard applications. This is related to the necessity for a low pressure drop and rapid heating, but also for the need of having a catalytic device which can be easily substituted. The necessity of having sometimes special forms as well as increasing gas–solid contact, even though maintaining a low pressure drop, stimulates research on alternative structured supports. Glass fiber panels [5] can be an interesting example in this direction. They are characterized by better efficiencies of gas–solid contact with respect to ceramic monoliths, low void fraction of the catalyst, and high flexibility to be adapted to different geometries. Active catalytic component dispersion and thermal stability, however, must be improved.

- Although the development of these devices often requires intense and interdisciplinary research (from surface science to catalyst preparation and engineering) which may appear not consistent with the initial small volume of the expected applications (therefore, a low economic return on the research investment), the catalysts often later are found useful in a much wider range of applications.
- Research on non-standard applications of environmental catalysts has mainly been carried out in catalyst producer companies, driven by customer needs. Academic interest in this area has often been limited, mainly due to the lack of specific funds for research. Consequently, there is a lack of fundamental background knowledge on the specific problems, but also the lack of a generalized approach in searching more systematically for possible applications. On the other hand, the public sensibility on the potential advantages of catalysis (lack of "visibility" of catalysis) is low. Being research mainly customer-driven (see above), it is evident that many potential areas of application of environmental catalysts are not explored and there is the need for public incentives to overcome this situation.

Other examples of non-standard applications of environmental catalysts were discussed during the workshop and some of them are also reported in this issue of *Catalysis Today*. Fu and Chen (Engelhard, US) discussed the design of cross-flow-channel monoliths for the control of odor and smoke generated from cooking processes. Berg and Berge (TPS Termiska Processer AB, Sweden) showed the results of field testing of catalysts applied to residential wood-fired boilers. Augugliaro et al. (Universities of Palermo and Turin, Italy) presented the behavior of different TiO_2 catalysts for the photocatalytic oxidation of hydrocarbon. Titania-coated tiles are currently under experimentation in various civil buildings in Japan like hospitals, etc. and in self-cleaning soundproof highway-walls, because the photocatalytic effect of TiO_2 allows the elimination of pollutants and also has an antibacterial effect [6]. Özkara et al. (Bogazici University, Turkey) discussed the behavior of low temperature CO oxidation catalysts based on Pt–SnO_2/alumina. These catalysts were initially discovered for the oxidation of traces of CO produced in a high power CO_2 laser (a space-based laser that uses carbon dioxide to help generate its beam; carbon dioxide molecules are decomposed into carbon monoxide and oxygen with a progressive loss in power of the laser), but their use can be extended to various applications in which room temperature CO oxidation is needed, such as in indoor air purification (the catalyst is effective not only in CO oxidation, but also in formaldehyde oxidation) or safety devices (e.g., laboratories using CO, etc.). Other applications include gas masks, submarine ventilation systems, and catalytic converters for cold-start emissions control of automotive exhausts.

Another application of low temperature CO oxidation catalysts is in the purification of H_2 to be used in proton exchange fuel cells (PEFCs). The presence of concentrations of CO higher than about 100 ppm poisons the Pt electrocatalyst of the fuel cell, but H_2 produced on board by steam or autothermal reforming of conventional fuels such as natural gas, gasoline or methanol followed by water gas shift conversion produces a mixture containing typically 1% CO or more. An efficient CO oxidation catalyst is thus necessary which should be highly selective, because H_2 oxidation should be minimized. In addition, catalysts for this purpose must be resistant to CO_2 and H_2O deactivation. Supported noble metal catalysts and in particular supported gold nanoparticles on transition metal oxides show interesting performances as discussed in the contributions of Grisel and Nieuwenhuys (Leiden University, The Netherlands) and Avgouropoulos et al. (ICE/HT and University of Patras, Greece).

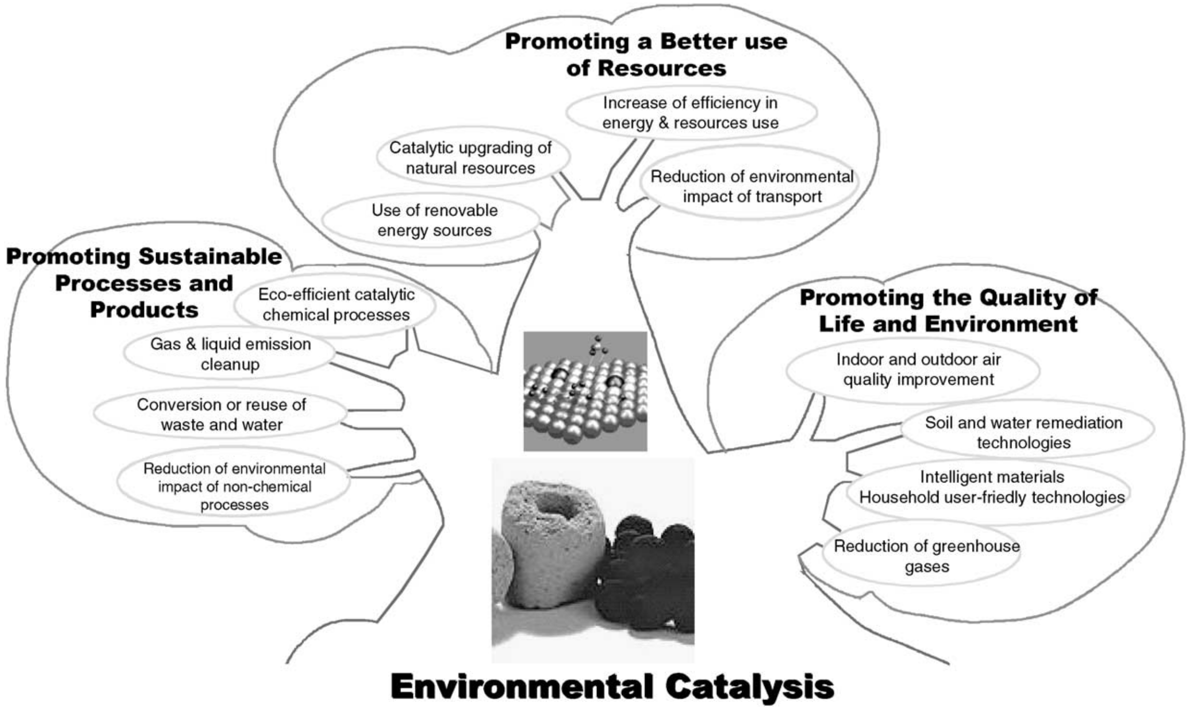


Fig. 2. The tree of the role of catalysis in promoting environment.

Other examples of non-standard applications of environmental catalysts include various household applications [7], such as (i) water purifier catalysts (based on MnO_2 supported on charcoal fibers) for Cl_2 and HClO removal, (ii) catalytic hair cutters and mosquito killers, (iii) deodorization apparatus for refrigerators, (iv) domestic catalytic combustors, (v) catalytic lighters for outdoor use, (vi) portable kerosene heaters and portable warmers and (vii) catalytic deodorization systems (e.g., to eliminate odors in toilets).

These examples well illustrate the concept of how environmental catalysis is expanding the range of catalysis use from chemical/energy fields to non-chemical, transport and daily life areas. Fig. 2 based on an original idea of Misono [4], summarizes this concept. The importance of this aspect is not only a broader market for catalysis, but also in terms of new challenges for research in order to overcome the often demanding constraints given by this expanded use of catalysts and in terms of increased social awareness that catalysis is a solution to improve quality of life.

4. Environmental catalysis as a driver for innovation

The extension of the use of catalysis outside the traditional fields together with the basic problem that often in the environmental technologies it is not possible to choose the optimal reaction conditions which are determined by energy and feed constraints and/or conditions defined by upstream units, implies that a very innovative effort is necessary to develop new catalytic materials, devices and solutions [8]. It is evident that the entire field of heterogeneous catalysis as well as other industrial sectors will benefit from this research effort, and not only the specific area of environmental catalysis.

For example, the ordinary conditions for use of heterogeneous catalysts in chemical syntheses are in the 200–500 °C temperature range, while environmental catalysts must operate sometimes at lower temperatures (room or lower temperatures, e.g., in the mentioned low temperature CO oxidation catalysts, in water purification technologies, or in some nitrogen oxides or VOC abatement systems, being too expensive the heating of large volumes of effluents) or at extremely high temperatures, 900 °C or above (e.g., in catalytic combustion for gas turbines).

Very high temperatures require developing catalytic materials having exceptional characteristics of stability and durability at high reaction temperatures. Various contributions in the workshop addressed this question, such as those of (i) Carroni et al. (ALSTOM Power, Switzerland) on the development of novel support materials for catalytic combustion in power generation, (ii) Groppi et al. (Polytechnic Milan, Italy) on understanding the reversible transformation of palladium in Pd-based catalysts for gas turbine combustors and (iii) Isupova et al. (Boreskov Institute of Catalysis, Russia) on honeycomb supported perovskite catalysts for high temperature processes.

Low temperature activity implies the development of novel, very active catalytic components or alternatively new ways to activate reactants or supply the energy required for the reaction. Some interesting advances in this direction were presented during the workshop. Miessner et al. (Institut für Umwelttechnologien in Berlin-Adlershof and Siemens AG, Germany) reported the application of non-thermal plasma (NTP) to assist catalytic cleaning of gas flows containing low concentrations of contaminants. NTP can be produced by a dielectric discharge reactor generating chemically active species, such as excited oxygen and nitrogen molecules, atoms and radicals like $OH^{\bullet}$ and $HO_2{}^{\bullet}$. Plasma assisted catalytic removal of NO_x may occur at temperatures lower than 100 °C, an important achievement for developing low temperature (<150 °C) catalysts for NO_x reduction in diesel engine exhaust emissions, although the application to mobile emissions (especially light-duty diesel engine cars) requires the resolution of various technical problems.

Barrault et al. (joint French contribution from LACCO, Poitiers; University of Paris; Centre de Resources Technologique Plasma Lasers, Orléans; Brandt Cooking, Saint Jean de la Ruelle) reported the combination of solid catalysts and dielectric barrier discharges to promote low temperature activity, but in VOC abatement. The field of application is generally the conversion of VOCs, but specific value can be found in the removal of odorous or toxic chemicals present in room temperature environments or emissions, and generally, when the VOC concentration is below the content to obtain an autothermic process.

The use of alternative oxidants such as ozone is another possible approach, as discussed by Ismagilov et al. (Boreskov Institute of Catalysis, Russia). Supported MnO_2 catalysts allow efficient conversion of toluene at temperatures below 100 °C, although catalyst deactivation a is a problem.

The question of ignition at room temperature of natural gas in order to develop no NO_x catalytic burners was addressed by Newson et al. (Paul Scherrer Institute, Switzerland) who showed that hydrogen assisted combustion allows a room temperature light off of methane and better control of hotspot temperatures which have a critical effect on catalyst life.

The question of promoting low temperature activity is also central to the development of diesel particulate abatement devices. Various contributions were given on this subject (e.g., by Moulijn et al., Delft University of Technology, The Netherlands; Ciambelli et al., University of Salerno, Italy; Pisarello et al., Sgo del Estero of Santa Fè, Argentina). Christensen and Rak (Dinex Filters Technology and ECN, The Netherlands) presented a novel concept of an electrochemical reactor consisting of a highly porous, oxygen ion conducting electrolyte (ceria–gadoline mixture) covered by a catalytically active, electron conductive perovskite (lanthanium strontium manganese perovskite) based electrode. The porous reactor structure acts as a mechanical filter, trapping the soot particles from the exhaust gas. By polarizing the reactor with an external power supply, the combustion process of the collected soot particles can be forced to take place at low temperature, where the lower temperature limit (250 °C) is defined by the ionic conductivity of the electrolyte material.

The concept of an electrochemically modulated catalytic device can be applied not only to promote low temperature activity, but also to develop systems having a variable and tunable activity, because, depending on the potential applied to the electrochemical reactor, the catalytic activity can be modulated. This allows developing “smart” catalytic devices having a variable activity driven by a coupled sensor. As mentioned above, the feed composition in various environmental applications may rapidly fluctuate. A temperature control is ineffective to follow these rapid fluctuations and thus overall efficiency can be low in these situations. The “smart” catalytic device concept is a potential solution to this problem, although research is in the beginning stages. The general scientific interest in developing “intelligent materials” may stimulate research in this area.

These examples, although not exhaustive of all recent technological innovations in the area of environmental catalysis, evidence the search for not-traditional solutions to solve the demanding problems addressed by environmental catalysis. The knowledge developed will have a positive impact on all the area of catalysis, but probably also a high inter-industry impact due to the interdisciplinary approach of the research.

5. Environmental catalysis promotes sustainable industrial chemistry

Industrial chemical processes from the beginning have moved towards a more efficient use of resources and an improvement of selectivity, because both aspects correspond to an improvement in process economics. Catalysis was a fundamental component of this innovation and therefore almost all new developments in catalytic industrial processes fall within the area of interest of environmental catalysis. Some relevant examples are reported in Table 1.

Various examples in this area were given during the workshop, but only a few are mentioned here in order to evidence some of the possible directions for innovation.

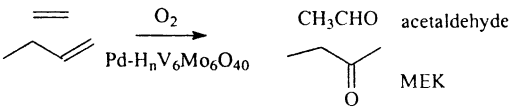
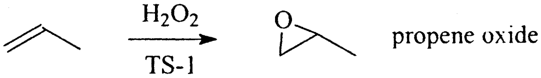
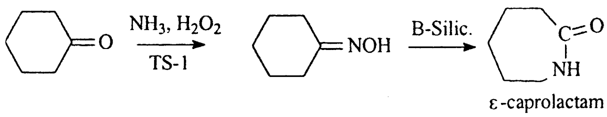
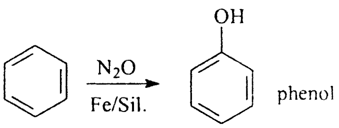
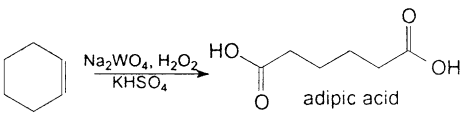
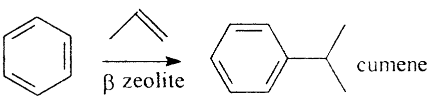
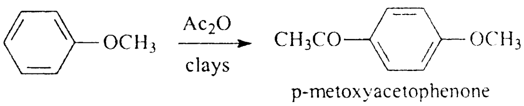
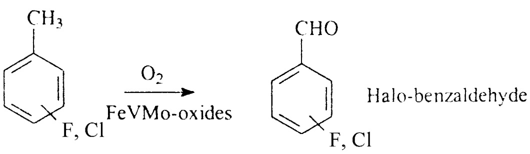
Eco-efficient processes in clean and unconventional media are one of the main areas of possible industrial innovation for environmental catalysis and sustainable (green) chemistry. Sanders et al. (University of Karlsruhe, Germany) reported on the behavior of sulfated zirconia (SZ) catalysts in the isomerization of butane in supercritical conditions. The behavior of SZ catalysts in *n*-butane isomerization is well known, but industrial application is hindered by fast deactivation due to cooking. Instead, using the catalyst under supercritical conditions (butane itself is the supercritical medium) makes it possible to maintain stable activity for a long time, due to the improved solubility power of the supercritical fluid for the coke precursor.

Process simplification is a challenge for all industrial syntheses, because it allows lowering of energy use, reduction of waste, and improvement of safety and process economics. Phenol is a large volume chemical because of its applications in various polymer syntheses. The conventional and commercial route is a three step process via cumene and cumene hydroperoxide. The alternative eco-compatible possibility is the direct synthesis by benzene hydroxylation made either in the gas phase using N_2O as the oxidant and Fe/ZSM-5 catalysts (Table 1) or H_2O_2 in the liquid phase using Ti- or Fe-zeolites (Kustov et al., Zelinsky Institute of Organic Chemistry, Russia). Another example of possible process simplification and improvement of eco-compatibility in an industrial synthesis of a large volume chemical is the gas phase selective oxidation of isobutene to methacrylic acid (Cavani et al., University of Bologna, Italy).

However, the largest potential for rapid industrial application of novel eco-compatible catalytic synthesis is in the area of fine or specialty chemicals, because large-scale production also requires large investments. Various possibilities of using catalytic synthesis in fine chemical production were reported by Barrault et al. (LACCO, Poitiers, France). Tichit et al. (Laboratoire de Matériaux Catalytiques des Montpellier, France) showed the possibility of “one pot” synthesis of dihydrocinnamaldehyde from benzaldehyde and propanal on Pd supported on a hydrotalcite catalyst. The process represents a substantial improvement over the three step conventional process which produces high amounts of effluents and salts. Kholdeeva et al. (Boreskov Institute of Catalysis, Russia; Silesian University of Technology, Poland) showed a new environmentally friendly method for the production of 2,3,4-trimethylbenzoquinone using Ti-containing mesoporous materials and H_2O_2 which avoids the formation of toxic and corrosive wastes. Other examples of “one pot” syntheses were given by Hölderich [9].

Hydrotalcite-based catalysts were also used as solid base catalysts in the alkylation of *m*-cresol with methanol (Cavani et al., University of Bologna and EniTecnologie, Italy) in order to develop cleaner processes alternative to homogeneous process. Lee et al. (Pohang University of Science and Technology, Korea) discussed the catalytic steps in the “green” synthesis of ibuprofen. Similarly, Trifirò et al. (University of Bologna, Italy) discussed different aspects of the catalytic steps in the greener synthesis of

Table 1
Examples of new eco-efficient catalytic processes

Process	Features
	Reduced formation of chlorinated waste
	Avoids chlorinated organic by-products (with respect to chlorohydrin process)
	Reduction of ammonium sulfate waste Avoids use of hydroxylamine
	Reduction of N_2O emissions (greenhouse gas) by reuse as reactant
	Production of N_2O is avoided Reduction of waste
	Reduction of polyalkylate waste
	Avoids use of hazardous catalysts, such as $AlCl_3$, BF_3 Reduced waste formation
	Reduced waste formation Reduced corrosion problems

ε-caprolactam. A “greener” synthesis of Nylon-6 is now possible [10].

The use of catalytic technologies may promote not only lowering of the environmental impact in chemical production, but also in other production areas. An example is given in the work of Kuznetsov et al. (Institute of Chemistry and Chemical Technology, Krasnoyarsk, Russia) who reported a new catalytic process for a sustainable chemistry of cellulose production from wood biomass.

Therefore, catalysis offers relevant possibilities for sustainable (green) chemical and non-chemical production [11,12], but an intensified effort is necessary for better identification of all opportunities, especially in non-traditional areas of catalysis.

6. Catalysis in waste minimization and emissions cleanup

Catalytic technologies have been traditionally applied to the purification of mobile and stationary emissions, but recently research has opened in new areas. Increasing attention has been given to the use of catalysis in polymer reuse and conversion, because the question of recycling or converting polymers has become a critical issue in recent years. Catalysis allows obtaining faster conversion and especially better (due to higher selectivity) quality of the products. Various contributions were presented at the workshop on this topic. Ali and Garforth (UMIST, Manchester, UK) reported on the different possible strategies for recycling polymer wastes and the role of catalysis to convert them to good quality fuels. Fernandes et al. (Federal University of Rio Grande do Norte, Natal, Brazil) showed the role of SAPO-37 zeolite in the catalytic degradation of high density polyethylene. Serrano et al. (Rey Juan Carlos University, Mòstoles, Spain) pointed out both the catalytic and reaction engineering aspects for the conversion of low-density polyethylene. Cardona and Corma (UPV-CSIC, Valencia, Spain) evidenced the possibility of using spent FCC catalysts for the catalytic cracking of plastic waste. Finally, Araujo et al. (UNESP, Araraquara and Federal University of Rio Grande do Norte, Natal, Brazil) discussed the role of MCM-41 catalysts in the conversion of low-density polyethylene.

Several contributions focused on the question of acid-catalyzed cracking of polymer waste to produce fuels, while none attempted the possibility of catalytic depolymerization, a better challenge towards the objective of polymer waste minimization and energy loss minimization. The area of use of catalysts in polymer conversion is thus an area of growing importance, but there are several basic fundamental questions that must be addressed regarding the nature of the catalyst and reactor technologies to be used. Furthermore, a broadening of the possibilities of using catalysts in these applications (e.g., basic catalysts for depolymerization instead of acid catalysts for cracking) is also necessary.

There are other important areas for application of catalytic technologies for solid waste conversion, such as (i) in the treatment of sludge (generally industrial sludge, but also for safe disposal of active sludge, a problem of increasing importance in Europe because the EU Urban Wastewater Treatment Directive has considerably limited the possibility of landfill disposal), (ii) the recycle of solid waste from chemical and refinery productions and (iii) in the treatment of fugitive emissions produced in solid waste treatments. Very few data are present in the literature on these questions, but their relevance will increase in the future.

Catalytic technologies in emissions cleanup (NO_x or SO_x elimination from mobile or fixed sources, VOC control) is one of the traditional areas of use of environmental catalysts, and considerable research is still being carried out on this topic. The main area of interest in recent years, well represented at the workshop, includes the development and testing of catalysts for (i) NO_x removal in lean burn or diesel engine emissions, (ii) catalytic combustion and (iii) VOC removal. The research attention was mainly focused on the study of the reaction mechanisms and the identification of the nature of the active sites. Also understanding the unsteady-state behavior has become increasingly important, due to the key role of this aspect in understanding the behavior of oxygen-storage components in three-way catalysts (TWCs) and the behavior of NO_x storage-reduction (NO_xSR) catalysts, the most promising solution to solve the issue of NO_x removal in light-duty diesel engine emissions. Different from conventional "steady-state" catalysts, these catalysts work continuously under periodic changes in feed composition from lean conditions (where NO_x is stored on the catalyst in the form of a nitrate) and rich conditions (where the stored NO_x species are reduced to N_2 by the H_2, CO and hydrocarbons present in the emissions).

The interesting concept on NO_xSR catalysts is the possibility of using a catalytic material with the double function of acting as a sorption material and a catalyst with periodic switching between the two functions. Another example of this concept is shown by the use of zeolite-based catalysts for VOC removal in rotating equipment. When the VOC concentration is low and the temperature of the emissions is also low (a typical example is the gas emissions from painting processes), the heating of large volumes of emissions to the temperature required for catalytic activity is expensive (if the VOC concentration is low, the heat of combustion cannot maintain the process autothermically). A solution is the use of a rotating monolith coated with zeolite-based catalysts which act as a sorbent when the monolith is in contact with the gas stream and as a catalyst in the other part of the monolith where the regeneration occurs. This is another example of the innovative and multifunctional possibilities of catalytic materials explored by environmental catalysis. Another example of this concept, but applied to the removal of pollutants in water (abatement of chloroorganics by adsorption on a bed of Pd/active carbon and in situ periodic regeneration by a reducing treatment) was given in the key note lecture of Y.M. Sheintuch (Technion-Israel Institute of Technology, Haifa, Israel).

7. Catalysis in indoor air quality improvement

Significant sources of pollutants may exist in indoor home and office environments [13]. Contamination arising from sources within the building include: (i) combustion products including carbon monoxide and environmental tobacco smoke, (ii) VOCs from building materials, fabric furnishings, carpets, adhesives, fresh paint, new paneling, and cleaning products and (iii) ozone from office equipment. These are five main sources of contamination:

- *Engineered wood products*. Indoor emissions from engineered wood products can arise from the base engineered wood, finishes applied to the wood, and glues used to hold the wood pieces together. The main chemicals detected are formaldehyde, toluene and aldehydes.
- *Photocopiers*. Office equipment, ranging from photoimaging machines, spirit duplicators, mimeograph machines, digital duplicators, and blueprint machines to computers and computer terminals and impact matrix printers have the potential to emit a variety of materials to the indoor air environment during their operational lifetimes. Pollutants of concern include VOCs, respirable particulates and ozone.
- *Circuit boards in computer monitors*. Paper base/phenol resin printed circuit boards (PCBs) used in computer monitors and boards may also be a relevant source of VOC emissions.
- *Cooking*. Various VOC (aldehydes, esters, hydrocarbons, aromatics, mercaptans, H_2S) and particulates or suspended aerosols, sometimes also with nasty odors, may be generated in the cooking of fish, meat and some vegetables.
- *Toilets and garbage disposal*. Nasty odors generated from methylamine mercaptans, fatty acids and amines, urea and uric acid.

In addition microbial contamination of ventilation systems or building interiors may generate indoor fungal aerosols, such as Stachybotrus Atra, Penicillium, Cladosporium and Aspergillus.

Catalytic technologies can play a relevant role in the improvement of indoor air quality due to these sources. For example, catalyst tablets to eliminate smoke and odors generated when fish or meat is cooked on barbeques are already commercial. Another catalyst is provided on top of an oil stove burner for complete combustion to eliminate the odor of aldehydes generated by imperfect combustion when the stove is extinguished [4,7]. A recent article on nanomaterials reported that gold particles 3–5 nm in diameter are very effective to remove odorous from toilets [14]. A Japanese company has since turned this effect into a product. Photocatalytic active titanium dioxide films can be used in reducing indoor air microbial contamination [6]. Formaldehyde can be eliminated on low temperature combustion catalysts.

However, this area in general has been little addressed in the scientific literature, although industrial interest is expanding, because it represent a potential interesting market. As outlined before, some contributions on this subject were presented during the workshop, even if not specifically focused on the objective of improving indoor air quality. Interest in this area must therefore be stimulated because it represents a new area of research for environmental catalysis.

8. Reduction of greenhouse gas emissions

The recent “European Climate Change Programme” (ECCP) of the European community has further stimulated the need for research in using catalytic technologies for greenhouse gas emissions control (CO_2, methane, N_2O, halogen compounds) [15]. This area is of increasing interest for the global effect of greenhouse emissions and for the increasing pressure to find realistic solutions to the problem.

Various contributions on this subject were presented at the workshop, although they addressed only part of the possible actions of catalysts in promoting the reduction of greenhouse gas emissions. For example, the use of CO_2 as a reactant in reforming reactions was presented by Gronchi et al. (Polytechnic of Milan, Italy), while Batiot-Dupeyrat et al. (LACCO, Poitiers, France) reported on the catalytic reforming of methane with CO_2. However, these reactions cannot be considered a technical solution to the problem of increasing CO_2 emissions, due to the orders of magnitude of difference in the dimensions of the problems. A novel reversible sorbent for CO_2 based on K_2CO_3/active carbon was presented by Okunev et al. (Boreskov Institute of Catalysis, Russia), but this cannot be considered a true catalytic technology. There are various interesting possibilities in the area of photo- and electro-catalytic conversion of CO_2, but they have received little attention in the area of environmental catalysis, differently from other areas such as that of electrochemistry. There are fundamental catalytic problems to be resolved in order to address the question of practical and effective photo- or electro-catalytic conversion of CO_2, although this knowledge should be integrated in an interdisciplinary approach. Increased effort in this direction is desirable in the future.

Various contributions focused instead on the question of N_2O removal from gaseous emissions. Generally, N_2O can be easily catalytically converted to N_2 at high temperatures (above 500 °C), but this has proven to be uneconomical in many practical cases. Furthermore, the presence of other gas phase components can considerably modify the reactivity. The question in the development of catalysts for N_2O conversion is thus not to develop only novel catalysts, but catalysts having the required activity at the reaction temperature necessarily based on economic considerations and in the presence of the other gas phase components in the emissions. In other words, the question of N_2O removal from gaseous emissions must be addressed with a clear reference to the practical cases. An interesting example in this direction was given by Van den Brink and Verhaak (ECN, The Netherlands) who presented the problematics of developing catalysts for the combined removal of N_2O and NO_x in the nitric acid industry. Fe-ZSM-5 catalysts are effective in this reaction when propane is added to the feed as a reductant, while methane in not very effective. Combination of Fe-ZSM-5 and a DeNO_x catalyst (based on Co-ZSM-5) in a single reactor gives more than 80% reduction of both N_2O and NO_x from the tail gases of nitric acid plants at 300 °C. Higher pressures are beneficial for N_2O and especially NO_x conversion. Another contribution on the question of N_2O reduction was given by Goncalves and Figueiredo (University of Porto, Portugal).

Various contributions on the question of methane combustion were given at the workshop, but generally the central question for application in the reduction of methane greenhouse gas emissions (e.g., low temperature activity with traces of methane) was not addressed. Various contributions focused on the use of non-traditional materials for methane oxidation, such as perovskites. Ciambelli et al. (Universities of Salerno, Naples and Rome; Italy) reported the behavior of La–Al–Fe perovskites for methane combustion. Perovskite-based monolithic reactors for the combustion of methane can also be developed (Cimino et al., University of Naples and Instituto Ricerche sulla Combustione CNR, Italy). These materials have been proven to be resistant in the presence of H_2S and SO_2 (Auer et al., University of Louvain-la-Neuve, Belgium) or sulfur compounds present in natural gas (Russo et al., Polytechnic of Turin, Italy) and were shown to be applicable for the treatment of "fugitive emissions" from the iron and steel making industry (Alifanti et al., University of Louvain-la-Neuve, Belgium).

The area of catalytic technologies for the reduction of greenhouse gas emissions is thus an area of growing importance, but still the need for research on one hand and the possibilities offered by catalysts on the other, must be better focused.

9. Catalytic water remediation technologies

Remediation of groundwater contaminated by agricultural practices (nitrate and pesticides, in particular), leakage of non-biodegradable compounds from underground fuel tanks and pipelines, and accidental spills and leaking of cleaning solvents and degreasers is becoming a major problem worldwide. "Europe's Environment": The recent reports of the European Environment Agency (EEA) "Dobris Assessment" and "Sustainable use of Europe's water?" highlighted the question that water pollution and deterioration of aquatic habitats are severely hampering the use of water for human consumption and wildlife. Inadequate amounts or poor water quality create a conflict between human demand for water and wider ecological needs.

It is estimated that the market for such technologies will double in the next 5–10 years, but that at the same time current available technologies are often inadequate to meet both economic and ecological demands. Therefore, there are both ecological and economic incentives to develop new technologies for water treatment and remediation. Catalysis may play a critical role in the development of these novel technologies, but this issue poses at the same time new challenges for catalysis. In water remediation, the challenge is that the catalysts must be able to efficiently operate on-site, which poses considerable constraints due to the fact that the technology must be compact (to be moved from site to site) and easily manageable.

Two major aspects of water remediation technologies were discussed at the workshop: (i) elimination of nitrate and pesticides from water contaminated by agricultural practices, and (ii) conversion of MTBE in contaminated underground water. However, various additional contributions were presented on the topics of (i) advanced catalytic wet oxidation technologies (of both organics and inorganics, such as ammonia), (ii) catalytic technologies of wastewater treatment by hydrotreating (including the key note lecture by M. Sheintuch, Technion-Israel Institute of Technology) and (iii) photocatalytic wastewater purification (coupling photocatalysts and membranes—Universities of Calabria and Palermo, Italy—and using TiO_2 photocatalysts for removal of cyanides—University Rey Juan Carlos, Spain).

Contributions on nitrate catalytic reduction in UK water were given by various research groups (Meytal and Sheintuch, Technion-Israel Institute of Technology; Chadwick et al., Imperial College, London and University of Belfast, UK; University of Venice, Italy; University of Poitiers, France; LACCO-CNRS of Poitiers, France). The catalysts were all based on Pd modified by components such as tin or copper, although different supports and reactor solutions were analyzed. However, the fundamental question of the formation of ammonium ions as by-products which should be less than 0.5 ppm for drinking water applications has not yet been resolved, at least on a practical scale.

The question of the conversion of MTBE (methyl *tert*-butyl ether) in contaminated water using zeolite catalysts was instead studied by Centi et al. (University of Messina, Italy). MTBE is a widely used gasoline additive, but its contamination of both ground- and surface-water has resulted in the ban of its use in California, recently. MTBE water contamination derives from leaking of underground fuel tanks and pipelines, tank overfilling and faulty construction at gas stations. While other gasoline components are characterized by good biodegradability and low water solubility (thus gasoline release shows a fast "natural attenuation" and low migration index), MTBE is very soluble in water (therefore, highly mobile in the ground water system) and resistant to biodegradation. Zeolites like H-ZSM-5 are effective catalysts for the room temperature conversion of MTBE in contaminated water to biodegradable chemicals. When H-ZSM-5 zeolite is added to an aqueous solution containing MTBE, there is fast initial adsorption after which slow decay begins with formation of alcohols as main products (*t*-butyl alcohol and methanol). Data indicate the practical possibility of using zeolites as catalysts for water remediation by MTBE contamination as well as a guard bed around gasoline tanks.

Water remediation technologies and in general the entire area of the use of catalysts in wastewater purification is thus a topic which will be of increasing importance in the future. In addition to the treatment of wastewater from chemical productions, other relevant areas are the reduction of the environmental impact of non-chemical (e.g., in the electronic, leather, tanning and pulp/paper industries) and agro/food productions.

10. Replacement of environmentally hazardous catalysts

The replacement of environmentally hazardous catalysts in existing processes and the disposal or reuse of spent catalysts are relevant industrial problems for sustainable chemistry and production, but have been rarely discussed in the literature. Some examples were given at the workshop. For example, Sahan et al. (UMIST, Manchester and Ciba Specialty Chemical, Clayton, UK) discussed the use of beta zeolite as a substitute for $AlCl_3$ in acylation reactions for fine chemical production. Chatti et al. (University of Tunis, Tunisia and University Catholique de Louvain, Belgium) discussed the use of hydrotalcite compounds as an alternative to caustic solutions. Other examples of more environmental friendly catalysts were also discussed.

It should be remarked, however, that very few data are available in the literature on the question of safe disposal of spent catalysts, a problem which is becoming of increasing relevance.

11. Conclusions

The scientific and market interest for environmental catalysis has significantly expanded in the last 2 decades, due to both the continuously increasingly more stringent regulations on the quality of emissions and the environment, and the increasing awareness of the central role that these catalysts play in the development of technologies to improve the quality of life and the environment.

The areas of interest of environmental catalysis have rapidly expanded, but at the same time new challenges for catalysis given by these new applications have stimulated research to find new innovative solutions and technologies which will benefit all areas of catalysis as well other industries.

The outlook is thus very interesting for research in the field of environmental catalysis. We hope that this overview, aimed at giving a general presentation of the topics discussed at the workshop "Environmental Catalysis: A Step Forward" (Maiori, Italy, May 2001) has provided a general perspective of the trends and outlook in this field and set the basis for a step forward in environmental catalysis research.

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