CATALYSIS FOR THE PROTECTION OF THE ENVIRONMENT AND THE QUALITY OF LIFE

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Keywords: Heterogeneous Catalysis for Environmental Protection, Three Way Catalysts, Catalytic Car Converters, DeNO$_x$ Catalysts, Volatile Organic Compounds, Catalytic Filters, Photocatalysis, Energy, Clean Fuels, Fuel Cells, Hydrogen

Contents

Summary

The role of catalysis in the reduction of the environmental pollution and in the improvement of the quality of life is discussed both in terms of end of pipe applications and pollution prevention strategies. This view is exemplified by presenting the key

applications of heterogeneous catalysis in mobile and stationary air de-pollution devices, in waste water treatments, in the development of clean new fuels, such as hydrogen and biodiesel and in the fuel cells development. Emerging catalytic technologies as well as problems related to the use of heterogeneous catalysts are also mentioned.

1. Introduction and General Aspects

The ability of a catalyst to increase the reaction rate by providing an alternative route of reaction with lower activation energy, is one of the essential principles utilized by the petrochemical, chemical and pharmaceutical industry since the XIX century. Despite its fundamental contribution to human development, the concept of catalysis reached the media and consequently the majority of the population only from late 1980's with the large scale introduction of environmental catalysts and in particular of the car converters. Nowadays it is well recognized that the use of heterogeneous catalysts significantly contributed to reduce the vehicles generated air pollution, even if this is not a completely solved problem, as we will see later. Currently, environmental catalysis is widely used in many important commercial sectors, with enormous benefits for the protection of the environment and for the improvement of the quality of our life. Heterogeneous catalysts are efficiently used to reduce nitrogen oxides (NO_x) emissions from stationary sources (power plants, boiler, …), to process oil in obtaining cleaner fuels having low sulfur and nitrogen content, to destroy waste, pesticides, dioxine and furane, to control the Volatile Organic Compounds (VOC_s) emissions an so on. More recently, environmental catalysts have been used to reduce water pollution, to oxidize organic particulate, to destroy ozone pollution in urban areas, to improve indoor air quality etc. Examples of industrial relevant applications of de-pollution heterogeneous catalysts are reported in Table 1. Nevertheless, it must be stressed that environmental catalysis acts in a more general scenario with the aim of the protection of air, water and soil also through prevention. It is in fact the base of the development of new and cleaner chemical processes, characterized by the use of safer reagents, by the production of a limited number and amount of by-products, by the elimination of production of dangerous intermediate and by the reduced mass and energy inputs requirements. Furthermore, heterogeneous catalysts are essentials to promote conversion of renewables / biomasses and in the production of cleaner fuels. Finally heterogeneous catalysis is becoming more and more important also in polluted soil decontamination.

Source	**Pollutants**	**Catalysts**	**Note**
Gasoline engines	Nitrogen oxides (NOx), hydrocarbons (HC_s) and carbon monoxide (CO)	Pt/Pd/Rh/$Ce_xZr_{1-x}O_2$/(La, Ba) –Al_2O_3 on ceramic and metallic monoliths	Stoichiometric air to fuel ratio
Diesel engines (light vehicles)	NO_X, HC_s, CO	Pt/Pd/Rh/BaO/Al_2O_3 on ceramic and metallic monoliths	Switch from oxidizing to reducing conditions
Diesel engines (heavy	NO_X, HC_s, CO	V_2O_x / TiO_2 on ceramic monolith	Use of ammonia or urea as reductant

vehicles, trucks and busses)		(NOx reduction), Pt, Pd / Al_2O_3 on ceramic and metallic monoliths (CO and HC oxidation)	
Diesel engines	Particulate	(i) Cerium and iron oxides (ii) Pt/ Al_2O_3 (iii) Cu, V and K based catalysts	(i) Ce or Fe fuel additives to generate in situ the catalysts during the combustion; (ii) the catalyst oxidises NO to NO_2, which then oxidizes the particulate
Power plants, gas turbines, waste incinerators	NO_x	V_2O_5-WO_3/TiO_2 on ceramic monolith	In the case of waste incinerators, simultaneous destruction of NOx and dioxins
Gas turbines	CO, HC_s	Pt, Pd / Al_2O_3 on ceramic and metallic monoliths	
Nitric acid production plants	NO_x	CuO-NiO/ Al_2O_3 o Cu-La/ Y	Possible partial conversion of N_2O
Nitric acid, adipic acid or caprolactame production plants	N_2O	Rh/Ce-ZrO_2, Rh/ hydrotalcites	Possible partial conversion of N_2O
Chemical plants, refineries, paintings, etc…	Volatile organic compounds (VOC_s)	Pt, Pd / Al_2O_3 on ceramic and metallic monoliths	
Refineries	H_2S, CS_2, COS	Al_2O_3 or TiO_2 (Fe_2O_3 / Al_2O_3)	Claus and Super Claus Processes
Waste water treatment from chemical, petrochemical, paper and electronic industry etc…	Organic compounds	Ru / TiO_2 ------------------------------------ TiO_2 (anatase)	Catalytic oxidation with air --------------------------------------- Photocatalytic process for diluted situations
Hospitals and public places	Organic compounds and bacteria	TiO_2 (anatase)	Photocatalytic process
Indoor air (houses and offices)	CO and odours	Nanostructured Au/TiO_2	Air purification
Indoor air (houses and	Formaldehyde	Pt, Pd/SiO_2	

offices)			
Aircraft cabin air	ozone	Mn or Pd/Al_2O_3	

Table 1. Examples of application of environmental heterogeneous catalysts.

2. Catalysts for Pollution Reduction from Mobile Sources

On September 14, 1967, the Council of Europe stated that "*the air pollution occurs when the presence of a foreign substance or a large variation of its components is liable to cause a harmful effect, according to the scientific knowledge of the time, or to create a discomfort*." This definition implies that some of the substances that we consider pollutants are minor components of the atmosphere (Table 2). Therefore local concentration effects must be carefully analyzed as well as global ones. For instance, the decrease of the ozone layer in the troposphere reduces the protective barrier from the UV radiation, while an increase of ozone concentration in the urban areas, due to photochemical processes induced by car pollution, is harmful for human health and promotes many oxidation / degradation processes, including the deterioration of plastic materials. The second important aspect is that the concept of pollution evolves with time as the scientific knowledge expands.

Finally, the general expression "*to create a discomfort*" implies that the pollutant can cause short- or long-term deleterious effects to human, animal or plant life or to the environment". Therefore pollution concern relates to a great variety of problems including bad odours or reduction of visibility caused by smoke of fog itself.

Constituent		**Constituent**	
N_2	78.084 %	NO	0.30 ppm
O_2	20.984 %	Xe	0.09 ppm
Ar	0.934 %	O_3	0.02-0.1 ppm
CO_2	0.034 %	CO	0.13 ppm
Ne	18 10^{-4} %	SO_2	0.002 ppm
He	5.30 10^{-4} %	NH_3	0.006 ppm
CH_4	1.70 10^{-4} %	C_2H_4	0.0002 ppm
Kr	1.14 10^{-4} %	H_2S	0.00005 ppm
H_2	0.50 10^{-4} %	CFCs	0.00015 ppm

Table 2. Average chemical composition of the atmosphere.

The contaminants which are directly emitted into the atmosphere are referred to as primary pollutants, while secondary pollutants are formed in the atmosphere by subsequent reaction of primary pollutants. Pollutant generated by combustion processes are currently a major cause of concern. The massive increase in the use of oil products in the internal combustion (IC) engines used in transportation has led to greatly increased problems of pollution in any urban area. Nowadays most cars are powered by a conventional-four stroke gasoline – burning internal combustion engine, but diesel engines are becoming more and more popular. These vehicles represent already about 30% of the light vehicles fleet and almost 100% of the heavy vehicles (busses, trucks…). The two systems substantially differ in the type of fuel (light hydrocarbons in the case of gasoline, long chain hydrocarbons in the case of diesel) and consequently in the fuel and air supplier systems and in the amount of oxygen supplied to the combustion chamber. In particular, diesel engines require to operate in the presence of a large excess of air to prevent the formation of particulate. More recently, four-stroke spark ignited lean-burn gasoline engines have been developed to enhance combustion efficiency and to reduce CO_2 emissions.

As reported in Table 3, the exhaust emission contains pollutants in various proportions depending on the type of engine. In particular, the incomplete combustion of the fuel leads to the emission of carbon monoxide (CO) and of unburned or partially oxidized hydrocarbons. These emissions are more significant when the oxygen concentration, even locally, is below the required stoichiometric ratio to reach full combustion. CO has a dramatic effect on human health as it can strongly coordinate to iron of the hemoglobin forming a compound 240 times more stable then that with oxygen. Therefore in its presence, even at ppm levels, the blood progressively reduces its ability of tissue oxygenation, up to the death. Particular dangerous are also the emissions of unburned or partially burned hydrocarbons (HCs), especially the aromatic or polycyclic ones, since those are or are suspected to be carcinogenic. Furthermore, the HCs can react with nitrogen oxides in a complex network of photochemical reactions which produce secondary pollutants, such as smog, ozone and peroxyl acyl nitrates. The presence of N_2 in the air and of N- and S-containing compounds in the fuel leads to the formation of NO_x and SO_x. These primary pollutants are also major responsible for the formation of acid rain, with the well known damage to the ecosystem and to the human manufactures, especially monuments. Finally there is an increasing attention to particulate matter (PM), since it easily reaches the deepest recesses of the human lungs. Especially fine particles, alone or in combination with other air pollutants, can cause respiratory problems, such as aggravated asthma, coughing and difficult or painful breathing, chronic bronchitis, shortness of breath capacity and in some cases premature death.

Exhaust Component [a]	Four-stroke spark ignited gasoline engine	Four-stroke spark ignited lean-burn gasoline engine	Diesel engine
CO_2	10 – 18 %	10-15 %	3-13 %
H_2O	10 – 12 %	10-12 %	1 – 7 %
O_2	0.2 – 2.0 %	0.6 – 7 %	5 – 15 %
CO	0.1 – 6.0 %	0.5-0.9 %	150 – 1200 ppm
NO_x	100 – 4000 ppm	800-2300 ppm	200 – 1000 ppm
HCs	400 – 5000 ppmC	350-1500 ppmC	10 – 330 ppmC
SO_x	15 – 60 ppm	10-50 ppm	10 – 100 ppm
PM	Low	Low	50-400 mg m^3
Temperature	RT-1373 K	RT-1173 K	RT-973 K
A/F (λ)	14.6-14.7 (~1)	40-30 (2.7-2); 14.6 (~1) [b]	45-18 (3-1.2)

Table 3. General characteristics of the exhaust emission as a function of the type of engine. * **(**Data from updated literature, most of them summarized from Kašpar J., Fornasiero P. and Hickey N. (2003). Automotive catalytic converters: current status and some perspectives, Catalysis Today, 77, 419-449. With permission.)

Already in 1910, a German law tackled the problem of environment pollution from mobile sources stating that "*the vehicles must be safe and built so as to preclude any nuisance for the public, by smoke or odor*". The chronic local pollution episodes experienced in California during the 1930's and early 1940's led to the introduction of the first legislative controls of auto emissions in 1947. However, only the introduction in 1966 of the US Clean Air Act, the first federal exhaust emission standards, and its subsequent amendments in 1968, 1970, 1971 etc., strongly and progressively forced the automotive manufacturers to reduce the emissions of the pollutants present in automotive exhausts. In the following years, most industrialized countries, first Japan, Canada and Europe, adopted similar legislations. After the introduction of these legislations, initial strategies to meet the first targets were based on prevention: engine modification allowed CO and HCs emissions reduction. In fact the air to fuel ratio influences the concentration of pollutants in the exhaust, as reported in Figure 1. The A/F ratio is expressed as the sometimes used equivalence ratio (λ λ). A value of $\lambda = 1$ $\lambda = 1$ indicates the point where the ratio is stoichiometrically balanced, i.e., when the amount of oxygen (air) present is that required by the fully combustion (to CO_2 and H_2O) of the fuel, corresponding to an A/F ratio (w/w) of 14.6.

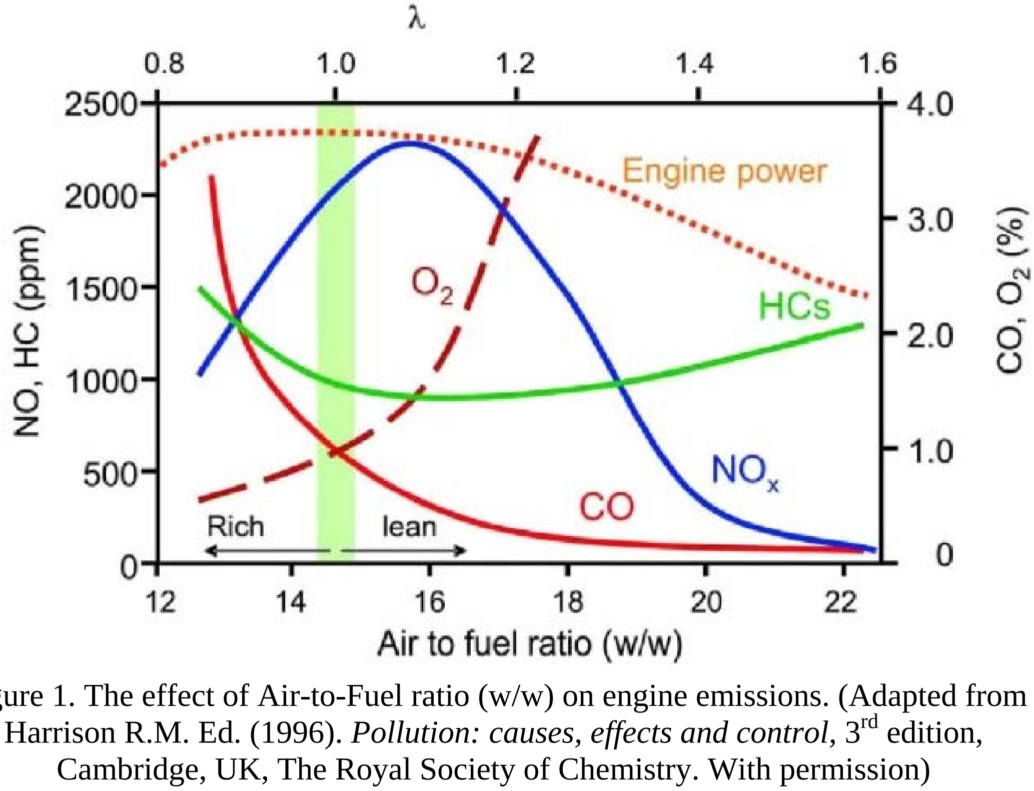

Figure 1. The effect of Air-to-Fuel ratio (w/w) on engine emissions. (Adapted from Harrison R.M. Ed. (1996). *Pollution: causes, effects and control,* 3rd edition, Cambridge, UK, The Royal Society of Chemistry. With permission)

When the spark-ignited gasoline engine is operating under rich conditions, i.e air to fuel ratios (A/F) below the stoichiometric ratio ($\lambda < 1$ $\lambda < 1$), the CO and HCs emissions are high while the NO_X emissions are low. This is because the deficiency in oxygen prevents complete fuel combustion. The concentration of NO_x is low since the adiabatic flame temperature is low. Increasing the A/F ratio results in a progressive optimization of the fuel combustion process, leading to lower CO and HCs emissions. However, a large excess of air with respect to the fuel ($\lambda \gg 1 \lambda \gg 1$), leads to an undesirable progressive engine power decrease, and ultimately, to combustion instability. Consistently, the unburned HCs emissions increase. NO_x emissions show a maximum slightly above the stoichiometric A/F ratio, as a result of the higher operative temperature of the engine and the high air content, which favors the recombination of oxygen and nitrogen to NO.

Figure 1 shows that there is no ideal ratio at which all the main emissions are low and the engine power is at acceptable level. A good compromise used in the seventies was to optimize the engine to run under lean conditions (oxidizing) in order to reduce the HCs and CO emissions. However, rather soon, the increasingly stringent limits required that end-of-pipe catalytic controls were introduced. In fact, only a catalytic system can efficiently convert the pollutants into harmless substances (NO, CO and hydrocarbons to N_2, CO_2 and water). Indeed, the development of the so called "car or catalytic converter" for gasoline engine represents probably the most successful large scale application of heterogeneous catalysts. Notably more and more stringent exhaust emission standards (limits) have been adopted not only for passenger cars, but also for light- and heavy-duty trucks (diesel engines). As an example, the uncontrolled CO emissions of passenger cars in the late sixties were around 60 g of CO km^{-1}, which dropped, according to the EURO4 -2005-EU limit, to less than 1.0 g km^{-1}.

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Biographical Sketch

Paolo Fornasiero was born in 1968 in Ruti (Switzerland). In 1992 he obtained the degree in Chemistry at the University of Trieste (Italy) and in 1997 he obtained his PhD in heterogeneous catalysis. After one year as post-doctoral fellow at the Catalysis Research Center of the University of Reading (U.K.), he was appointed assistant professor in 1998 and associate professor in 2006 in Inorganic Chemistry at the University of Trieste. His scientific interests are the technological applications of material science and heterogeneous catalysis directed to the solution of environmental problems, such as the design of innovative materials for catalytic converters, the development of catalysts for the reduction of nitrogen oxides under oxidizing conditions, the combustion of diesel particulate, and the design of new catalysts for the production and purification of hydrogen to be used in fuel cells. He is coauthor of 110 publications on international journals, four patents and a number of communications to national and international meetings, in many cases as invited lecturer. He was awarded in 1994 the Stampacchia Prize (a national Prize to young chemist for his first scientific publication) and received the Nasini Gold Medal in 2005, awarded by the Italian Chemical Society, for his contribution to the research in the field of inorganic chemistry.