Chapter 8

CATALYSTS FOR CONTROL OF EXHAUST EMISSIONS

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8.1 INTRODUCTION

The application of catalysts to control emissions of CO, NO_x, and reactive hydrocarbons from automobiles began in the U.S. in 1975. Catalytic control of NO_x from electricity generating power plants started in Japan and West Germany at about the same time. As a measure of the present importance of catalysts for emissions control, it is noted that of the $1900 million annual sales of catalysts in the U.S., sales of catalysts used for emissions control are larger than either catalysts used for petroleum refining or for chemicals manufacturing.

Environmental problems are becoming of increasing importance. Nonpolluting production and use of energy fuels is now considered to be one of the most serious challenges faced by mankind. Environmental protection is an integral component of every energy technology. To be successful, a new process must be both economically and environmentally superior. Energy-related environmental problems involve several topics: acid rain, global warming and the deleterious effects on crops and human health caused by ground-level ozone. Chemicals of concern as atmospheric pollutants are SO_x, NO_x, CO, CO_2, O_3 (ozone), and volatile hydrocarbons. The interactive chemistry of these atmospheric pollutants is complex, particularly since ozone is a product of secondary reactions. In summary, ozone is formed as the result of a sequence of photochemical and radical reactions between O_2 and CO, or O_2 and hydrocarbons in which NO_x is critically involved in intermediate reaction steps (Seinfeld, 1991).

The application of catalysts for prevention and abatement of NO_x is now discussed, particularly in the utility industry. Then catalytic control emissions in the transportation sector is addressed.

8.2 CATALYTIC PREVENTION AND ABATEMENT OF NO_x POLLUTION

Among the developing efforts for effective NO_x control technologies, the most notable are: combustion modifications; selective catalytic reduction systems; catalytic decomposition of nitrogen oxides; and three-way automotive catalysts.

8.2.1 Catalytic Combustion to Prevent NO_x Formation

In a conventional flame operated at high temperature with air, NO_x is formed to an appreciable extent since the equilibrium concentration of NO_x from nitrogen and oxygen increases at higher temperatures, particularly above 1500°C (Figure 1). Combustion of natural gas for application in a high temperature turbine can raise temperatures to 1600°C, resulting in unwanted NO_x

levels. Catalytic fuel combustion, which can operate effectively at lower temperature than thermal combustion, is being tested as a means of *preventing* No_x formation. Turbine temperatures are limited to about 1300°C due to limitations in construction materials. In present operation, air is added to the combustion gases to bring the turbine inlet gas temperature to this level. Addition of this amount of air before combustion would lower temperatures and result in unacceptably slow combustion. The concept is to speed up combustion to acceptable rates by the use of a catalyst, while keeping the temperature at 1300°C. One example of such a system is illustrated in Figure 2 (Garten, 1992).

The effect of various combustion systems on NO_x and CO concentrations is illustrated in Figure 3. If we think of the results of using a conventional flame combustor, which gives somewhere between 400 and 2,500 ppm NO_x in the flue gas, it is easily recognized that the catalytic combustion system gives markedly lower values than the flame combustor. Also, the catalytic combustor gives lower concentrations of CO, which leads to a slower ozone formation rate.

Thus, the use of a catalytic combustion can provide many advantages. The temperature in the catalytic combustion systems can be maintained at lower temperatures where the equilibrium NO_x is negligible. Also, the ignition temperature to start combustion can be lower and combustion can proceed in a stable manner.

Catalytic combustion is, accordingly, one of the promising technologies to be developed in the future. However, there are many problems to be solved. These include providing catalysts which are thermally stable and provision of materials and design combinations to achieve sustained performance at high temperatures.

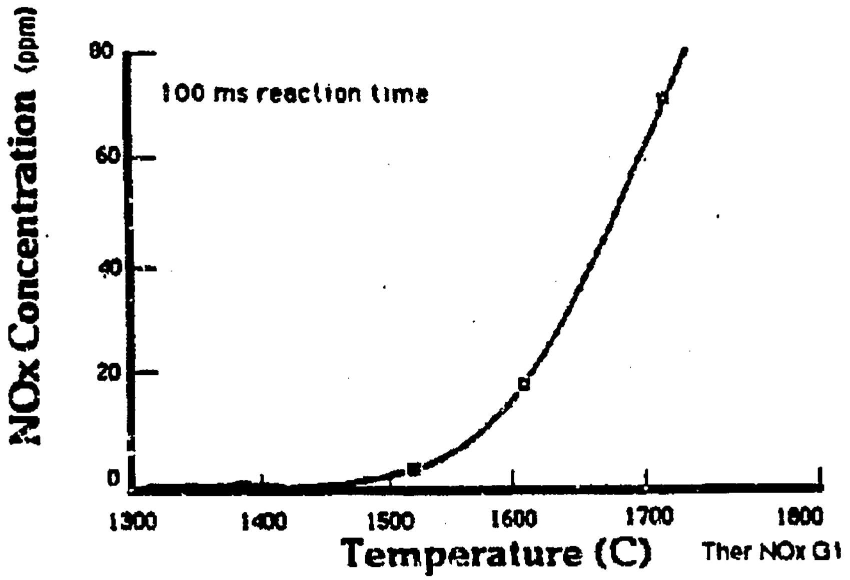

Figure 1. **No_x Formed in Premixed Homogeneous Combustion.** (Cusumano, 1992)

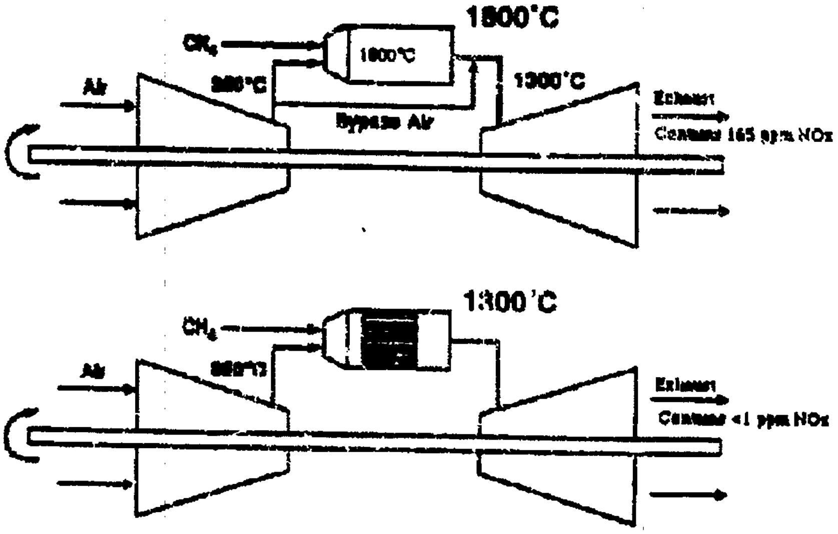

Figure 2. Gas Turbine Options. (Garten, 1992)

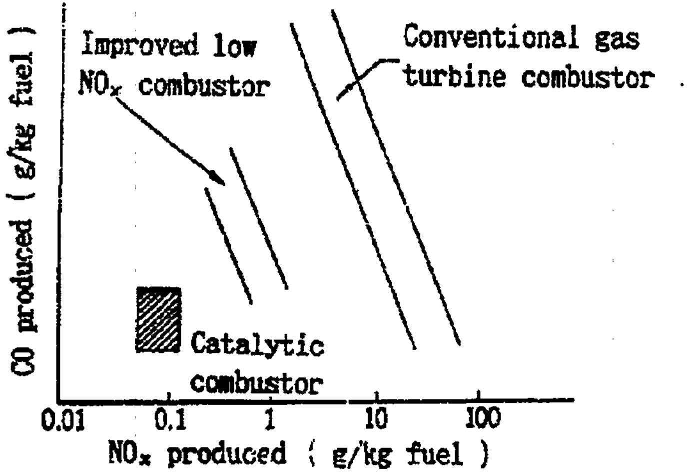

Figure 3. The Abatement of NO$_x$ Production by Means of Catalytic Combustor.

8.2.2. NO_x Remediation by Selective Catalytic Reduction, SRC

8.2.2.1 Catalytic Reduction of NO_x by Ammonia

Stationary sources of NO_x far outweigh cars and trucks as major sources of generation of NO_x. At present, control of NO_x emissions from electric utility plants is carried out commercially by selective catalytic reduction by ammonia. Commercial installations are widespread in Japan and Western Europe (Austria, Germany, Holland, Scandinavia, and Switzerland) where technology was developed (Bosch and Janssen, 1987). Ammonia is added to combustion gases to achieve 90-9[illegible] NO_x removal by the reaction

$$O_2 + 4NO = 4NH_3 \rightarrow 4N_2 + 6H_2O .$$

A vanadia/titania catalyst is used in a parallel flow-through honeycomb catalytic structure. In some instances, silica is included in the catalyst formation. WO_3 or MO_3 may replace part of the V_2O_5. *A key to the success of the V/Ti catalyst is that it is not poisoned by SO_2 under* operating conditions as are platinum catalysts which were developed earlier. Design by computer modelling has been used to achieve a 50% improvement in catalytic volumetric activity to optimum pore structure control. (Beckman and Hegedus, 1991).

However, there is need for catalyst improvements. Sulfur oxides contained in the flue gas cause problems. SO_2 is converted to SO_3 which react to form sulfates which plug catalyst pores and cause erosion and corrosion. Further as the catalyst deteriorates, the activity at a fixed NH_3/NO_x ratio decreases and the slippage of NH_3 increases, with resultant discharge of NH_3 into the atmosphere. Increasing the NH_3/NO_x ratio increases activity but further increases slippage. Research is needed to understand better the fundamental nature of active sites and reaction pathways in order to make improvements in this developed technology.

8.2.2.2 Catalytic Reduction of NO_x by Hydrocarbons in the Presence of Oxygen

Reduction of NO_x by hydrocarbons has recently attracted much attention internationally as a possible new denitrification process for exhaust gases from utility plants and from diesel and lean-burn gasoline engines. Catalysts comprised of copper ion-exchanged on zeolite ZSM-5 were the first discovered to be active and selective for reduction of NO_x under oxidative conditions. (Held *et al.*, 1990; Iwamoto *et al.*, 1990). Intensive research at numerous laboratories has been reported at recent symposia, (Tokyo, 1990 and San Diego, 1994). Research has focused both on fundamental catalytic chemistry and on the applications testing of a variety of catalysts.

Much debate has ensued on the role of hydrocarbons in the selective reduction of NO_x under oxidizing conditions. Various schemes have been proposed, namely; a) a redox mechanism involving Cu(I), generated through reduction by hydrocarbon, b) oxygenated hydrocarbons as reaction intermediates, and c) deposition of catalytically active carbonaceous materials which react further with NO. Isocyanate species, - NCO, have been postulated as intermediates in NO-C_3H_6-O_2 dynamic behavior. The reaction between nitro compounds and NO_2 has been proposed as the main route of N_2 formation for NO-C_3H_6-O_2 on Ce-ZSM-5 catalysts.

A wide variety of catalyst compositions has been tested under practical conditions for NO_x reduction by hydrocarbons. Performance capabilities have been established for catalysts fabricated by ion-exchanging zeolites with Cu, Co, Ni, Ce, Rh, Ga, and In (for example, Li and Amour, 1993; Jen *et al.*, 1994).

It has been shown that Ce/Sr-ZSM-5 has high activity under a wide range of conditions due to the efficient utilization of hydrocarbons. Gallium-containing catalysts have a high activity under a wide range of reaction temperatures (Yogo *et al.*, 1993).

NO_x reduction depends a great deal on the hydrocarbon used. The performance of olefins, methane, propane isobutane, have been reported (Gopalakrishnan *et al.*, 1993; San Diego, 1994). Hydrocarbon emissions from a gas-cogeneration system, such as an electric power plant, are comprised mainly of CH_4 Therefore, it would be advantageous to develop a catalyst which is active for reduction of NO_x by CH_4 in oxygen-rich atmospheres (Armor and Li, 1994; Zhang *et al.*, 1994).

Catalyst support components other than zeolites of the ZSM-5 type have also be investigated. Metals ion-exchanged on ferrierites are very active catalysts for the reduction of NO_x in the presence of oxygen (Li and Armor, 1993).

Platinum-group metals catalysts are also regarded as promising. Supported on gamma alumina, they displayed high NO_x conversion activities when tested in real diesel exhaust gases, especially at relatively low temperature between 200° and 350°C. It is claimed that they have higher activity and durability than Cu-ZSM-5 catalysts under real diesel exhaust conditions (Obuchi *et al*, 1993).

At present, while scientific and technological progress is very promising, no commercial process has been developed for catalytic reduction of NO_x under oxidative conditions. This is regarded as a high priority research topic.

A prime motivation to develop such technology, as discussed in the next section, is that lean-burn engines, which operate at high air/fuel ratios, have the ability to provide higher fuel efficiencies. Three-way automotive catalysts have been successful in controlling exhaust emissions from conventional automotive engines which operate under stoichiometric air-fuel conditions. However, the exhaust from lean-burn gasoline and diesel engines contain over 5% oxygen. Under these not-oxidizing conditions the 3-way catalysts are no longer effective for NO_x control. There is a real research need for alternative catalyst systems for lean-burn gasoline and diesel engines.

8.2.3 Catalytic NO_x Decomposition

The decomposition of NO_x to harmless nitrogen and oxygen is one of the most challenging topics in removing NO_x from exhaust gases. As discussed above, thermodynamics informs us that at lower temperatures NO_x should be decomposed to its constituents elements, which are nitrogen and oxygen. Accordingly, the catalytic decomposition of NO_x could become the simplest and cheapest method for removal of NO_x from combustion exhaust gases.

Since Jellinik first studied catalytic decomposition of NO in 1906, many materials have been examined for NO decomposition. The following systems have been found to be the most active: supported nobel metals such as platinum; the silver-cobalt oxide system; perovskite systems; and metal exchanged zeolites such as Cu-ZSM-5. Of all the known NO decomposition systems studied so far, copper-exchanged ZSM-5 is the most active.

However, present catalysts are not active enough at commercial conditions (Catalytica, 1993). Furthermore, the Cu-ZSM-5 catalyst is inactivated for NO decomposition by the presence of sulfur dioxide, although it remains active for catalytic reduction of NO (Iwamoto *et al.*, 1991).

New approaches are needed. For example, a novel solution to NO_x reduction has been tested using a corona discharge applied to electrodes with catalytic coatings that promote the favorable $2NO \rightarrow N2 + O2$. NO_x decomposition was achieved. Currently higher energy efficiency is being sought, necessary for commercialization (Suhr *et al.*, 1990.)

8.3 CATALYSIS FOR CONTROL OF AUTOMOBILE AND TRUCK EMISSIONS

8.3.1 Controlling Automobile Emissions

Automobile exhaust emissions are determined by fuel composition, engine design and operation and by catalytic converters located in the exhaust system. Exhaust gases from spark-ignition automobiles contain harmful CO, NO_x, and hydrocarbons (incompletely and partially combusted fuel constituents). As discussed in Seinfeld (1991), NO_x reacts photochemically with reactive hydrocarbons to form ground-level ozone and also contributes to acid rain formation. SO_x also appears in auto exhaust gases to the extent that the fuel contains sulfur.

Automotive converters using oxidation catalysts were introduced in the U.S. in 1975, converting CO and unreacted hydrocarbons to CO_2 and H_2O. Three-way automotive converters catalyze these oxidation reactions and also simultaneously reduce nitrogen oxides. They have been widely adopted to meet federal NO_x standards, beginning in 1981.

Catalysts for automotive emissions control are now well developed and, in general, are capable of meeting presently mandated U.S. standards for CO, NO_x, and HC emissions from auto exhaust pollutants compared with those built 25 years ago, before emissions control (Taylor, 1990). However, the 1990 CAAA requires significantly greater future reduction than is now mandated. Required is reduction of NMHC (non-methane hydrocarbons) to a maximum of

0.125 gm-per-mile (down from 0.41 in 1991), CO to 1.7 gm-per-mile (down from 3.4 in 1991), and NO_x to 0.2 gm-per-mile (down from 1.0 in 1991). Further, auto catalytic converters must remain effective for 100,000 miles, up from 50,000 miles.

California has set in place a program of future emissions standards much more stringent than the 1990 CAAA including requirement than 10% of new cars have "zero" emissions. This is tantamount to requiring electric cars.

Thus, the U.S. has set in motion the necessary legislation to remove autos as a serious source of air pollution in the 21st century and beyond. This legislation is research-forcing since technology is not now available which is considered to be economically and technically satisfactory.

In seeking to reach acceptable air quality and to determine where emphasis should be placed, it has been recognized that the diminution of pollution from autos is less than anticipated from control regulations. From a study of emissions inventory, the less-than-expected results (about half as well as expected) have been largely attributed to certain autos with high emissions rates (Calvert *et al.*, 1993). Most of the mobile source emissions are by a small percentage of vehicles. Half the CO and HC emissions come from 10% of the vehicles. Some are older vehicles. However, unexpectedly, high emission rates are detected from a few modern autos due to tampering or other reasons. It has been noted that motor vehicles are now responsible for less than half urban NO_x emissions into the atmosphere. Hence, major reduction in NO_x from stationary source emissions should also be considered.

Automobile pollution control necessarily interrelates fuels composition, engine combustion performance and catalytic converter remediation systems (Armor, 1992). As far as engines are concerned, it is clear from Figure 4 (Acres, 1991) that NO_x formation is linked to CO and HC control. Figure 5 (Acres, 1991) describes the effectiveness of NO, CO, and HC control by the Pt/Rh catalyst as a function of the optimal stoichiometric air/fuel ratio (equivalence ratio, λ). In addition, fuel economy and maximum power vary considerably with air-fuel ratio. Major steps have been taken by auto manufacturers to accomodate to the requirements for efficient operation of converter catalysts (Taylor, 1993).

Modern 3-way converter catalysts control CO and HCs by oxidation. Simultaneously NO_x is removed by reduction according to the equations:

$$2CO + NO \rightarrow 2CO_2 + N_2 \quad \text{and} \quad HC + NO \rightarrow CO_2 + H_2 + N_2$$

The generic converter catalyst structure was invented in the early 1950s (Houdry, 1952). Catalytic materials in automobile converters are generally supported on a ceramic honeycomb monolith. The honeycomb, made of cordierite ($2MgO.2Al_2O_3.5SiO_2$). contains 200-400 square channels per square inch and is coated with an activated alumina layer called the wash coat.

Catalytic Pt, Pd, and Rh are highly dispersed on the high area wash coat. Rh metal displays high activity for the removal of CO, HCs, and NO_x and is particularly important for reduction

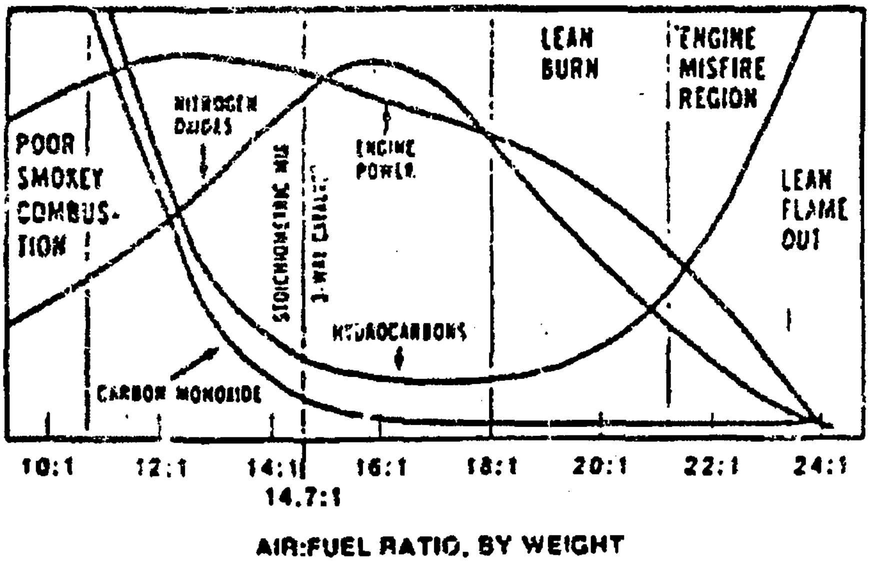

Figure 4. The effect of air/fuel ratio on engine operations. (Acres, 1991).

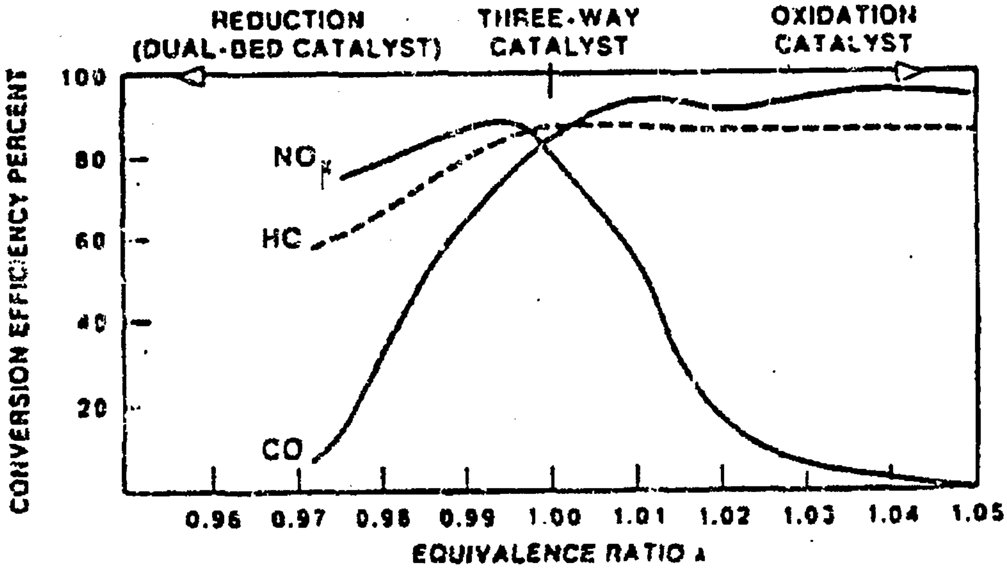

Figure 5. The effect of exhaust gas stoichiometry on the conversion efficiency of a rhodium/platinum catalyst. *(Acres, 1991)*.

of NO_x. Fresh Pd is more active than Pt in most cases for these three pollutants but is more susceptible to poisons such as lead and sulfur and sinters rather easily in a reducing atmosphere. Ceria may be added at a loading of 2-30 wt.% to the washcoat of three-way catalysts to storeoxygen to promote the water-gas-shift reaction, and to stabilize the nobel metals against thermal damage (Taylor, 1990). Nickel can be added to scavenge H_2S.

Although it is estimated that 96% of the exhaust HC and CO and 76% of the NO_x can be eliminated by the use of catalytic converters, there are needs and opportunities for improvements, discussed by Farrauto *et al.* (1992) and other authors referenced in this section. Three-way catalysts operate near the stoichiometric air-fuel combustion ratio and exhaust temperatures are normally 400-600°C. However, today's catalytic converters do not reach minimum operating temperatures until about 100 seconds after cold start of an automobile. During this warm-up period, more than 50% of NHHC and CO emissions pass unreacted. The problem of cold-start pollution has been addressed by seeking to provide special procedures and catalytic apparatus.

- Electrical preheating the catalyst, which requires the honeycomb monolith that supports it to be made not of ceramic but of a metal that can withstand temperatures up to 1000°C.
- Moving the catalyst nearer the engine manifold, where temperature is higher, would also heat the converter faster. This move would expose the catalyst to higher temperature during use.
- Use of a starter catalyst placed near the exhaust manifold, which can be coupled with the primary catalytic converter in the conventional location.
- Use of a hydrocarbon storage device, a unit upstream from the converter which prevents hydrocarbons from passing unreacted through the converter by adsorbing them when the catalyst is cold and releasing them to the catalyst when it has reached operating temperature

Catalyst reformulations offer several opportunities for improvements.

- There is a need for increased catalyst longevity - specifically resistance to sintering at high temperature and resistance to poisons (P, Zn, S).
- There is a desire to use precious metal more efficiently, particularly rhodium which is expensive and in limited supply.
- Effective catalytic decomposition of NO_x remains a key need.

Fuel composition is an integral factor in emissions control.

- It has been recently demonstrated that even low levels of sulfur in gasoline can be critical to converter efficiency. The sulfur emissions lowers the catalytic activity of the converter.
- Lowering fuel vapor pressure would assist in lessening HC emissions.
- Alternative fuels, including oxygenates, can be attractive since they are potentially less polluting.
- It has been pointed out by Bertolacini (1992), that a 'perfect' converter catalyst would make a choice of fuels not limited by inefficiencies of the converter. Thus, from a combustion viewpoint there would be no need to limit fuel aromatics which have useful octane enhancement properties and certain manufacturing advantages.

There is an important opportunity to improve *fuel efficiency* by raising the air-to-fuel ratios from current stoichiometric ratio of about 14.6 to between 18 and 21. Unfortunately, current three-way catalysts cannot reduce NO_x to N_2 in the more highly oxidizing environment. What is needed is an effective 'lean' NO_x reduction catalyst. The lean nitrogen oxides reduction system must be closely integrated with the engine so that the exhaust stream will have the type and amount of hydrocarbons needed to reduce these oxides. Promising research has identified CuZSM 5 catalyst combinations but they are not yet sufficiently active and stable (Armor and Li, 1994).

If catalytic technology can be developed that removes NO_x effectively when gasoline-fueled spark-ignition engines are operated lean (that is with high air-fuel ratio), significant *fuel efficiency gains* could be made. Research is recommended to explore the *application of catalysts in engines* capable of removing NO_x under lean-burn conditions with the objective of increasing fuel efficiency and environmental protection.

8.3.2 Controlling Truck Emissions.

Exhaust gases from diesel engines contain particulates - primarily soot, liquid hydrocarbons, and sulfates - in addition to CO, NO_x, and volatile HCs. Liquid hydrocarbons consist of unburned fuel and lubricating oil. Sulfur oxides are formed from sulfur contained in the fuel. Even though sulfur in diesel fuel will drop to 0.05% in 1994 from current 0.15-0.13%, significant amounts of sulfur oxides will still be present in the exhaust. It is expected that exhaust aftertreatment will be needed for soot, liquid organics, and for sulfur abatement. Research has been focussed on filters to remove soot, and on oxidation catalysts to remove liquid organics and on preventing sulfate formation (Farrauto *et al.*, 1992).

In the region in diesel engines where plenty of oxygen is present, thermal NO_x is formed, whereas in the oxygen-deficient region, carbon-containing particles or soot are formed in a heterogeneous manner. One of the ways of abating NO_x is to modify the engine to lower the temperature of the oxygen-excess region by slowing the rate of fuel supply, which may on the other hand, result in an increase in soot formation and may decrease fuel efficiency. Diesel converter catalysis technology complements diesel-engine technology. The focus is on reducing NO_x formation in the engine with the expectation that carbonaceous material can be dealt with via catalytic aftertreatment.

The lean-burn type engine, to which the diesel belongs, works under excess air conditions and exhibit high energy efficiency, but on the other hand emit considerable amounts of NO_x in the exhaust gases in the presence of excess air. One of the ways to alleviate NO_x emissions would be direct catalytic decomposition of NO_x to its constituent elements, N_2 and O_2, but in most cases the decomposition is inhibited by the presence of excess oxygen since it is more strongly adsorbed on the catalyst surface than NO_x. On the other hand, the catalytic reduction of NO_x by hydrocarbons is accelerated by the presence of oxygen (Held, 1990; Iwamoto *et al.*, 1991; Obuchi *et al.*, 1993) and accordingly may become a good method for abating in the presence of excess oxygen. It is an important task to selectively reduce NO_x and also to improve the thermal stability and life of catalysts, in particular, susceptibility to coexisting gases and vapors such as steam and sulfur compounds.

It should be noted that alternative fuels could reduce particulates and other pollutants for diesel engines. Compressed natural gas and methanol are beginning to be used in city buses in several cities. Even though these fuels are cleaner burning, catalysts are still needed to lower CO, NO_x, and HC emissions.

The discussion of environmental protection by catalysis, the subject of this chapter, is augmented by the presentation of the research status and opportunities in applications chapters.

8.4 RESEARCH NEEDS

- Pursue an understanding of the chemistry of pollutant formation and remediation.
- Develop technology to abate ozone pollution by:
  - Catalytic removal of ozone at sites where its formation is high.
  - Decreasing introduction of NO_x into the air.
- Develop catalysts to:
  - Achieve combustion at lower temperatures where formation of NO_x does not occur.
  - Catalytic decomposition of NO_x to nitrogen and oxygen at practical rates.
  - Improve selective reduction of NO_x.
- Explore the application of catalysis for removing NO_x under lean-burn engine conditions with the objective of increasing fuel efficiency and environmental protection.

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