

## CHAPTER III

### THEORY

The development of the spark-ignited combustion engine permits the controlled combustion of the gasoline that provides the power to operate the automobile. Gasoline, which contains a mixture of paraffins and aromatic hydrocarbons, is combusted with controlled amounts of air to produce complete combustion products of CO<sub>2</sub> and H<sub>2</sub>O [20].



and also some incomplete combustion products of CO and unburned hydrocarbons (HC). The CO level ranges from 1 to 2 vol.%, while the unburned hydrocarbons are from 500 to 1,000 vppm. During the combustion process, very high temperatures are produced by diffusion burning of the gasoline droplets, resulting in thermal fixation of the nitrogen in the air to form NO<sub>x</sub> [21]. Levels of NO<sub>x</sub> are on the 100 to 3,000 vppm range. The exhaust also contained approximately 0.3 moles of H<sub>2</sub> per mole of CO. The quality of pollutants varies with many operating conditions of the engine but is influenced predominantly by the air-to-fuel (A/F) ratio in the combustion cylinder. Figure 3.1 [22] shows the engine emissions from a spark ignited gasoline engine as a function of the air-to-fuel (A/F) ratio [22].

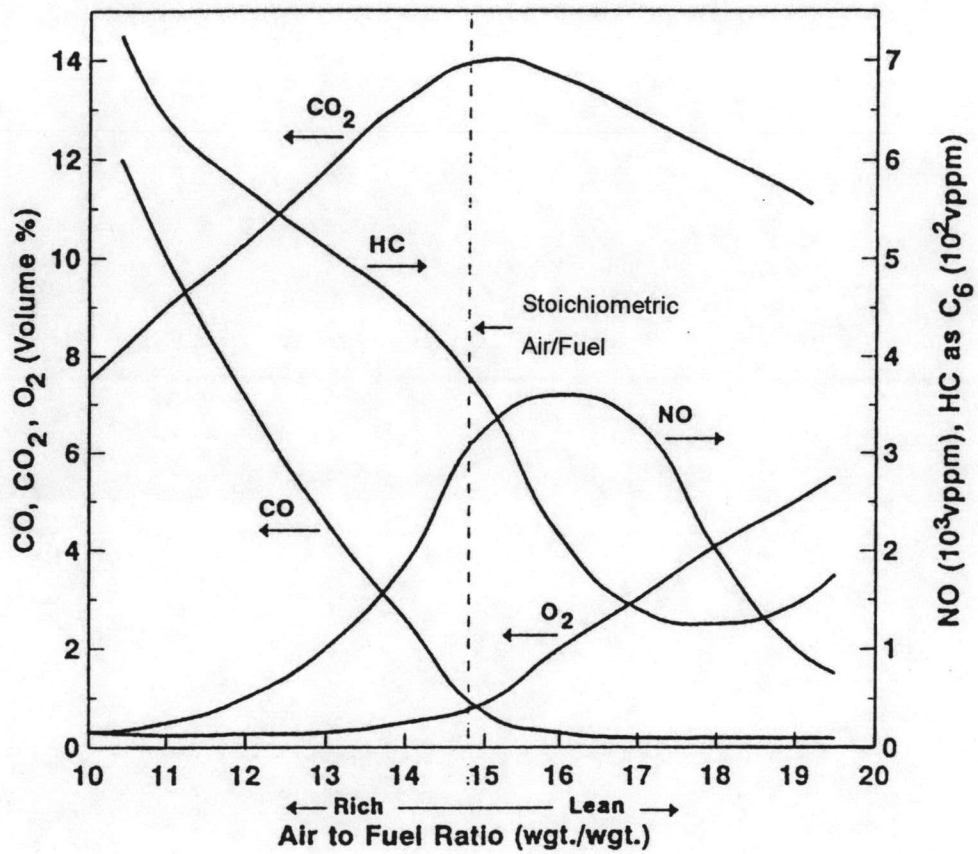


Figure 3.1 Spark-ignition gasoline engine emission as a function of air-to-fuel (A/F) ratio [22].

When the engine is operated rich of stoichiometric, the CO and HC emissions are highest while the NO<sub>x</sub> emissions are depressed. This is because complete burning of the gasoline is prevented by the deficiency in O<sub>2</sub>. The level of NO<sub>x</sub> is reduced because the adiabatic flame temperature is reduced. On the lean side of stoichiometric, the CO and HC are reduced because nearly complete combustion dominates. Again, the NO is reduced because the operating temperature is decreased. Just lean of stoichiometric operation, the NO<sub>x</sub> is at maximum, since the adiabatic flame temperature is the highest. At stoichiometric, the adiabatic flame temperature is lowered because of the heat of vaporization of the liquid fuel gasoline. The actual operating region of combustion for the spark-ignited engine is defined by the lean and rich flame stability, beyond which the combustion is too unstable [23].

Within the region of operation of the spark-ignited engine, a significant amount of CO, HC, and NO<sub>x</sub> is emitted into the atmosphere. The consequences of these emission have been well documented [24]. CO is a direct poison to humans, while HC and NO<sub>x</sub> undergo photochemical reaction in the sunlight, leading to the generation of smog and ozone.

The three main major pollutants could be listed as following:

#### 1. Unburnt hydrocarbons (HC)

HC is emitted from various sources such as factories, petroleum tanks (stationary sources) and automobiles (mobile sources). Non-methane HC is one of the main substances to cause photochemical reaction. As suggested by Figure 3.1 [22], when the mixture is leaned excessively, the HC levels increase because of incomplete combustion. Either the mixture is

too lean to support combustion, or the temperature is too low, or both. During a cold start, unburned hydrocarbon results from excess fuel or fuel enrichment in the combustion chamber. This fuel is present in the cylinder to initiate combustion. An overall rich A/F produces high levels of HC [25].

## 2. Carbon Monoxide (CO)

Automobile exhaust gas is the main source of carbon monoxide air pollution. Though concentrations have decreased meanwhile, carbon monoxide is still a problem because not much was known about its chronic effect and because it contributes to the climatic effect as its greenhouse potential is five times that of CO<sub>2</sub> [26].

High concentrations of CO, as shown in Figure 3.1 [22], are discharged from an engine operating at rich A/F ratio. As A/F ratio approaches the stoichiometric value, the CO concentration never drops to a very low value. Some CO persists even at a lean overall A/F ratio because of cylinder-to-cylinder distribution sufficient time to reach equilibrium of oxidation of CO to CO<sub>2</sub>.

According to non-equilibrium chemistry, CO is an intermediate product in the oxidation reaction of hydrocarbons. Unburned hydrocarbons are present even in lean mixtures, and the partial oxidation of some of the unburned hydrocarbons can produce CO [26].

## 3. Nitrogen oxides (NO<sub>x</sub>)

Air pollution in the form of nitrogen dioxide (NO<sub>2</sub>) is understood to be originated from the oxidation of N<sub>2</sub> materials. Although the direct product of such combustion is mostly nitrogen monoxide (NO), this substance undergoes



oxidization in the air to become  $\text{NO}_2$ . Sources of the emission of  $\text{NO}_2$  are industrial plants, motor vehicle, commercial establishment, homes etc.

Nitrogen oxides, together with hydrocarbons, play an important role as precursors for tropospheric ozone and photochemical smog [27]. Ozone is toxic gas for both man and animals. It reduces lung function. Ozone affects plants, in particular in combination with other air pollutants, like  $\text{NO}_x$  and  $\text{SO}_2$ -synergistic effects can be observed, entailing higher damages than one pollutant alone, e.g. reduction of harvest. Tropospheric ozone affects the climate by contributing to the greenhouse effect.

$\text{NO}_x$  output from an engine is also very sensitive to A/F ratio, as shown in Figure 3.1 [22], with the peak production occurring at an A/F ratio slightly lean from stoichiometric. Unfortunately, the A/F ratio for maximum  $\text{NO}_x$  production is usually close to both the A/F ratio for minimum HC production, and the A/F ratio for low CO production. Because NO production is associated with high temperatures, very little  $\text{NO}_x$  is produced during the cold start, in contrast to the large HC and CO outputs from a cold start.

### **3.1 The exhaust gases composition [28]**

In an ideal case, an engine receives a stoichiometric mixture of fuel and air, and completes the combustion process to carbon dioxide, water vapor, and nitrogen. The stoichiometric mixture for a typical fuel consist of 14.7 parts by weight of air to one part of gasoline. In actual practice, an engine is designed to produce lean mixtures (such as 16:1) for best fuel economy while the car is cruising at medium speed. The engine is also

designed to produce rich mixtures (such as 12:1) in order to prevent stalling during idling and cold start, and to produce maximum power during acceleration and very high speed cruising. The combustion process is never complete, so that the exhaust gas will contain carbon monoxide, hydrocarbons, hydrogen, and a number of oxygenated compounds such as aldehydes. Some of the nitrogen in the air will combine with oxygen to form oxides of nitrogen during high temperature oxidizing conditions in the cylinders. Exhaust gas pollutant concentrations depend mainly on air-to-fuel ratios, as shown in Figure 3.1 [22].

A large variety of hydrocarbons is found in the exhaust gases. The molecules with six or more carbon atoms represent unreacted gasoline. For instance, engines operating with platforming gasoline give the highest percentage of aromatics in the exhaust gas, and engines operating with catalytically cracked gasoline give the highest percentage of olefins. The very large quantity of olefins and paraffins with three or fewer carbon atoms indicated considerable cracking. The composition depends somewhat on the driving mode. According to the modes of city driving, the operation ranges of an engine (range of torque and rotating speed) vary, as well as the nature of the work performed. As a result, the quantities of exhaust emissions also vary as follows.

$$\begin{aligned}
 \text{exhaust emission quantity} &= (\text{exhaust emission concentration}) \\
 &\quad \times (\text{exhaust gas flow rate}) \times (\text{driving time})
 \end{aligned}$$

The concentration of respective emissions and the exhaust gas flow rate during the above four kinds of driving modes vary generally as shown in the Table 3.1 [26].

Table 3.1 Exhaust emission concentration and exhaust gas flow rate at each driving mode [26].

Driving Modes	Emission Concentration	Exhaust Gas Flow Rate
Idling	CO and HC are high, and NO <sub>x</sub> is low	Low
Acceleration (car starting or passing)	CO, HC and NO <sub>x</sub> are high	High
Constant speed	CO and HC are low, and NO <sub>x</sub> becomes higher at a higher speed	High at a higher speed
Deceleration	CO and HC, especially HC, are high, and NO <sub>x</sub> is low	Low

At present driving situation of the urban areas receiving much traffic volume of large cities, most driving is done at speeds of less than 40 km/hr [26]. Moreover, there are many starts and stops due to traffic signals and traffic jams, which make exhaust emission levels depend on idling, acceleration and deceleration greatly. In heavily congested traffic, when average speeds are low, the quantities of all three of the above exhaust emissions are high, but decrease to a minimum at speeds between 30 to 40 km/hr.

A similar trend is also noticeable in terms of fuel economy. The average speed in urban districts when 30 to 40% of the total running time is consumed by idling is mostly 10 to 20 km/hr. Therefore, the idle adjustment of the engine greatly effects CO and HC emission levels. Exhaust emission standards in Japan specify the permissible levels of CO and HC concentrations for idling of vehicles in use [24]. The composition of the exhaust gas emitted during the process of burning a mixture having an A/F ratio in the stoichiometric ratio is illustrated in Table 3.2 [26].

Table 3.2 The composition of exhaust gas emitted on the mixture in the vicinity of stoichiometrical air/ fuel ratio is burnt [26].

Name of material	Volume rate (% or ppm)
N <sub>2</sub>	83.5 (%)
O <sub>2</sub> (including argon)	2.22 (%)
CO <sub>2</sub>	13.0 (%)
H <sub>2</sub>	0.23 (%)
CO	0.97 (%)
HC	205 (ppm)
NO	2900 (ppm)
NO <sub>2</sub>	18 (ppm)

Remark :- Fuel is gasoline at Air/fuel ratio 14.7

- All values have been measured without regard to water content and 1 (%) = 10,000 ppm



The exhaust gas composition for the various driving modes of spark ignition gasoline engine is summarized in Table 3.3 [29] as follows:

Table 3.3 Typical Exhaust Gas Composition Spark Ignition Engine 1.8 l [29].

Operation conditions	Idling	Partial load	Full load
Torque (Nm)	0	26	114
Torque (%)	0	23	100
Rotational speed( $\text{min}^{-1}$ )	900	3000	5000
Temperature ( $^{\circ}\text{C}$ )	280	505	910
Space velocity (NI/h)	5760	27,100	123,950
Linear velocity (m/s)	0.54	3.6	25.2
Residence time (s)	0.3	0.045	0.006
O <sub>2</sub> (Vol%)	1.17	0.8	0.43
NO <sub>x</sub> (Vol-ppm)	162	1850	2670
HC (Vol-ppm)	689	514	380
CO (Vol%)	0.76	0.68	1.05
H <sub>2</sub> (Vol%)	0.25	0.22	0.35
SO <sub>2</sub> (ppm)	6.4	6.4	6.4
CO <sub>2</sub> (Vol%)	14.1	14.7	14.6

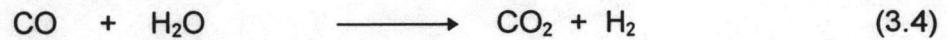
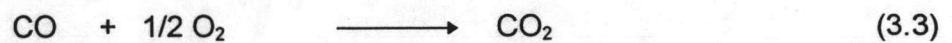
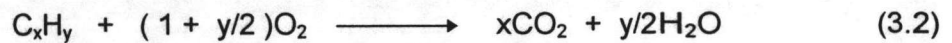
Residual : Nitrogen, water, and vapor



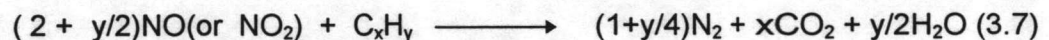
### 3.2 The catalytic reaction for pollution abatement [20]

The basic operation of the catalyst is to perform the following reactions in the exhaust of the automobile [20]:

#### *Oxidation of CO and HC to CO<sub>2</sub> and H<sub>2</sub>O*



#### *Reaction of NO/NO<sub>2</sub> to N<sub>2</sub>*



The underbody location of the catalytic converter in the automobile is shown pictorially in Figure 3.2 [30]. When a driver first starts the automobiles, both the engine and catalyst are cold. As the exhaust gradually warms, it reaches a temperature high enough to initiate the catalytic reactions. This is referred to as the light-off temperature, and the rate of reaction is kinetically controlled; that is, it depends on the chemistry of the catalyst because the transport reactions are fast. Typically the CO reaction begins first, followed by the HC and NO<sub>x</sub> reactions. When the vehicle exhaust is hot, the chemical reaction rates are fast, and the overall conversions are controlled by pore diffusion and/or bulk mass transfer.

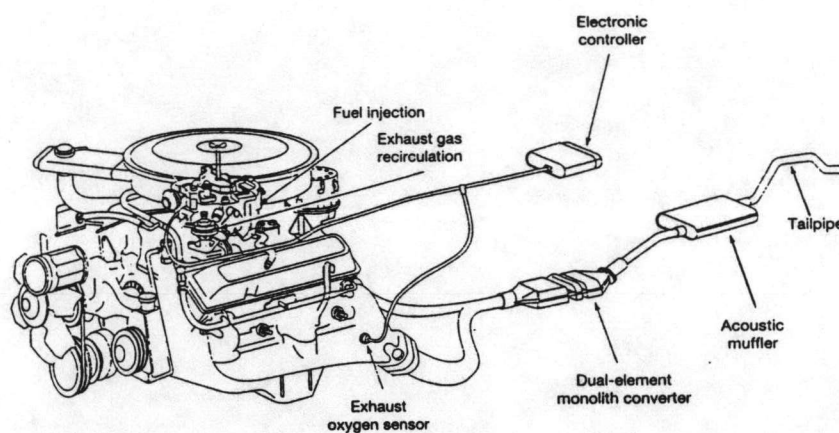


Figure 3.2 Location of a catalyst in underbody of an automobile [30].

### 3.3 Making the finished catalyst [31]

#### 3.3.1 Impregnation

The most common commercial procedure for dispersing the catalytic species within the carrier is by impregnation an aqueous solution containing a salt (precursor) of the catalytic element or elements [32]. Most preparation simply involve soaking the carrier in the solution and allowing capillary and electrostatic forces to distribute the salt over the internal surface of the porous network. The salt generating the cations or anions containing the catalytic element are chosen to be compatible with the surface charge of the

carrier to obtain efficient adsorption or, in some cases, ion exchange. For example,  $\text{Pt}(\text{NH}_3)_2^{+2}$  salts can ion exchange with the  $\text{H}^+$  present on the hydroxy containing surfaces of  $\text{Al}_2\text{O}_3$ . Anions such as  $\text{PtCl}_4^{-2}$  will be electrostatically attracted to the  $\text{H}^+$  sites. The isoelectric point of the carrier (the charge assumed by the carrier surface), which is dependent on pH, is useful in making decisions regarding salts and pH conditions for the preparation.

#### 3.3.1.1 Incipient Wetness or Capillary Impregnation

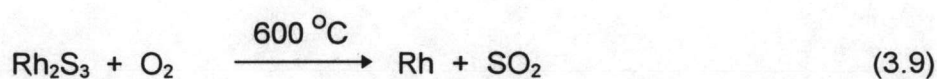
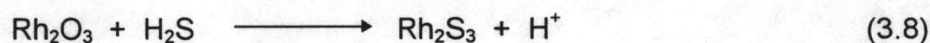
The maximum water uptake by the carrier is referred to as the '*water pore volume*'. This is determined by slowly adding water to a carrier until it is saturated, as evident by the beading of the excess  $\text{H}_2\text{O}$ . The precursor salt is then dissolved in an amount of water equal to the water pore volume. Once dried, the carrier pore structure is certain to contain the precise amount of catalyst species.

#### 3.3.1.2 Fixing the Catalytic Species

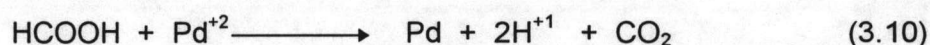
Following impregnation, it is often desirable to fix the catalytic species so subsequent processing steps such as washing, drying, and high-temperature calcination will not cause significant movement or agglomeration of the well dispersed catalytic species.

The pH of the solution is adjusted to precipitate the catalytic species in the pores of the carrier. For example, by presoaking  $\text{Al}_2\text{O}_3$  in a solution of  $\text{NH}_4\text{OH}$ , the addition of an acidic Pd salt, such as  $\text{Pd}(\text{NO}_3)_2$ , will precipitate hydrated PdO on the surfaces of the pores within the carrier. In some selected cases,  $\text{H}_2\text{S}$  gas can be used as a precipitating agent. After

all the preparation processing steps, the catalyst is treated at high temperature in air to decompose and drive off the sulfur. This method has been used in the fixing of Rh onto  $\text{Al}_2\text{O}_3$  in automobile exhaust catalyst [31].



An alternative approach is the addition of reducing agents to precipitate catalytic species as metals within the pore structure of the carrier.



This method is particularly effective for the precious metals because they are easily reduced to their metallic states. The advantage of the reducing agents mentioned above is that, upon subsequent heat treatment, they leave no residue [31].

### 3.3.1.3 Drying

Excess water and other volatile species are removed during forced air drying at about  $110\text{ }^\circ\text{C}$ .

### 3.3.1.4 Calcination

It is most common to calcine the catalyst in forced air to about  $400\text{--}500\text{ }^\circ\text{C}$  to remove all traces of decomposable salts used to prepare the catalyst.

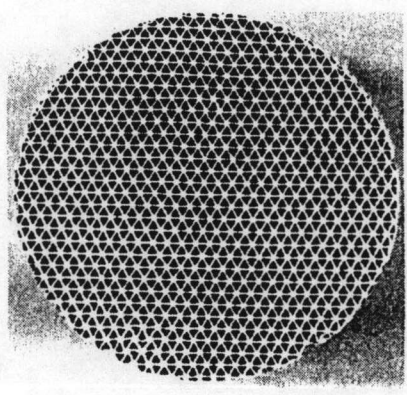




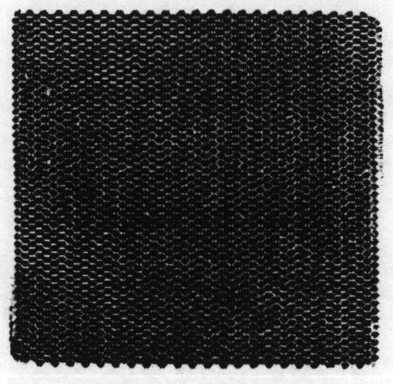
### 3.4 Monolithic Materials as Catalyst Substrates [31]

Monolithic or honeycomb materials offer a number of advantages over more traditional pellet-shaped catalyst and, thus, are now widely used as support in environmental applications. It is a unitary structure composed of inorganic oxides or which may be square, sinusoidal, triangular, hexagonal, round, and so on. Five types of monolithic honeycombs are shown in Figures 3.3 [31]. A triangular channels is shown in Figure 3.3a, whereas a layered honeycomb steel structure with hexagonal shaped channels is shown in Figure 3.3b. A square-channels extruded ceramic with 400 cells per square inch (the most commonly used for automotive applications) is shown in Figure 3.3c. A layered steel structure, also with sinusoidal channels, is shown in Figure 3.3d and a metallic monolith wound in an S-shape, with sinusoidal channels, is shown Figure 3.3e.

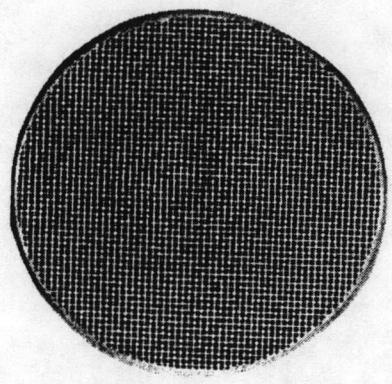




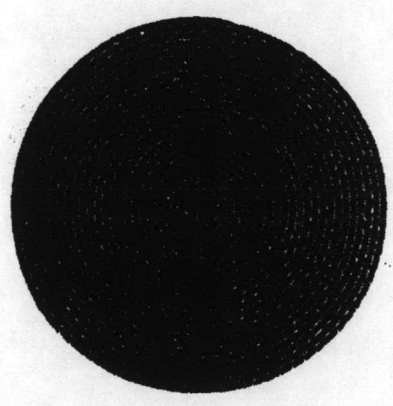
a.)



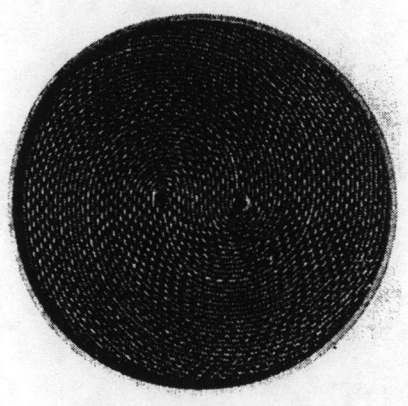
b.)



c.)



d.)



e.)

Figures 3.3 Monolithic supports [31].

Commercial ceramic monoliths have large pores and low surface areas (i.e.,  $0.3 \text{ m}^2/\text{g}$ ), so it is necessary to deposit a high surface area carrier, which is subsequently catalyzed, onto the channel wall. The catalyzed coating is composed of a high surface area such as  $\text{Al}_2\text{O}_3$  and impregnated with a catalytic component such as Pt. This referred to as the *catalyzed washcoat*, illustrated in Figure. 3.4 [31]. The washcoat can be seen deposited over the entire wall, but it is concentrated at the corners of the square-channel ceramic monolith. The thickness of the 'fillet' depends primarily on the geometry of the channel and the coating method. The pollutant-containing gases enter the channels uniformly and diffuse to and through the washcoat pore structure to the catalytic sites where they are converted catalytically.

Monoliths offer a number of design advantages that have led to their wide-spread use in environmental applications such as catalytic converter used for automotive emissions control. However, the most important is the low pressure drop with high flow rates. The monolith which has a large open frontal area and with straight parallel channels offers less resistance to flow than that of pellet-type catalyst. Low pressure drop translates to lower compressor costs for stationary applications and greater power for mobile sources. Other advantages are excellent attrition resistance, good mechanical properties, compact, freedom in reactor orientation, and so on.

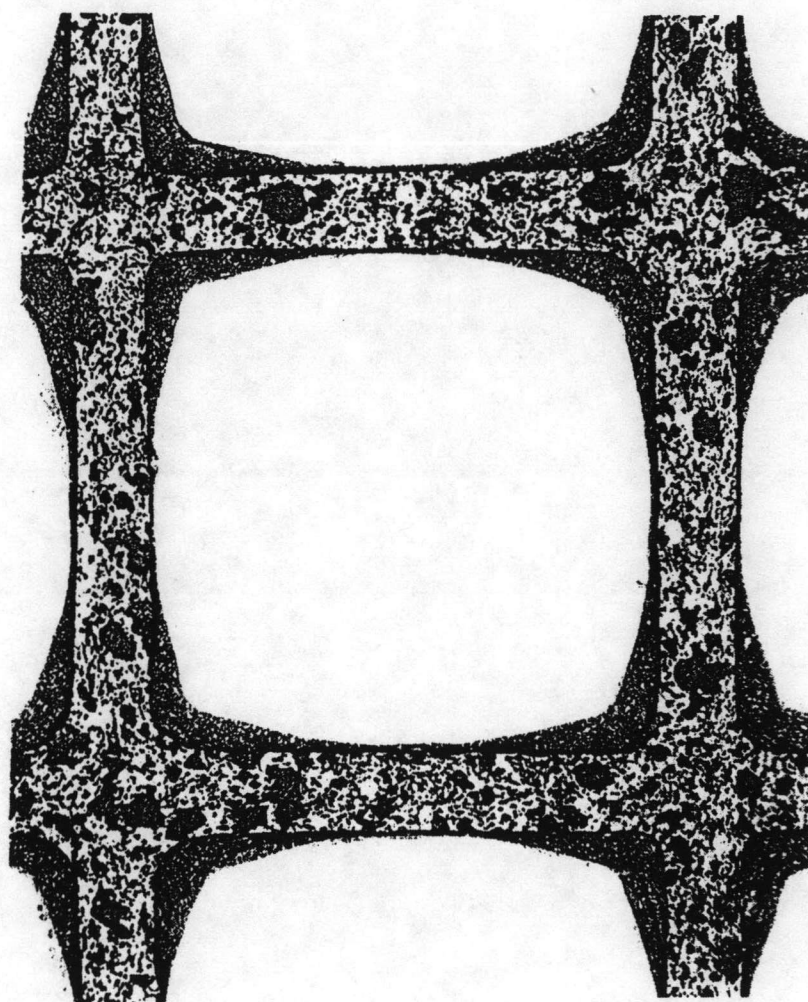


Figure 3.4 Ceramic monolith coated with a catalyzed washcoat [31].



### 3.4.1 Ceramic Monoliths

The monolithic supports are made of alumina and related materials such as cordierite ( $\text{Al}_4\text{Mg}_2\text{Si}_5\text{O}_{18}$ ), mullite ( $(3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)_2$ ), spumene ( $\text{LiAl}(\text{SiO}_3)_2$ ), and asbestos ( $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$ ) [28].

Synthetic cordierite, the first mentioned above, is by far the most commonly used ceramic for monolithic catalyst support applications [30]. Raw materials such as kaolin, talc, alumina, aluminium hydroxide, and silica are blended into a paste and extruded and calcined. It is possible to produce sizes up to about 11 inches (27.94 cm) in diameter and 7 inches (17.78 cm) long, with cell densities from about 9 to 600 cells per square inch (cpsi). The conversion desired, the physical space available for the reactor, and engineering constraints such as pressure drop are considered when designing the monolith size [33].

Cordierite monolith possesses several important properties that make this material preferable for use as a support. These properties are described below [31].

#### Thermal Shock Resistance

By nature of its low thermal expansion coefficient ( $10 \times 10^{-7}/^\circ\text{C}$ ), cordierite undergoes little dimensional change when cycled over a wide temperature range. Thus, it resists cracking due to thermal shock.

The washcoat influences the thermal shock resistance of the monolith (especially during rapid temperature changes) because it expands more than the monolith. Particle size of the carrier and thickness of the washcoat are two key parameters that must be optimized.

### **Mechanical Strength**

Monoliths are made with axial strengths of over 3,000 pounds per square inch (psi). They must be resistant to both axial and mechanical perturbations experience in automotive, truck, and aircraft applications. The high mechanical integrity is derived from the physical and chemical properties of the raw materials and the final processing after extrusion.

### **Melting Point**

The melting point of cordierite is over 1300 °C far greater than temperatures expected for modern environmental applications. The materials are also resistant to harsh environmental such as high temperature steam, sulfur oxides, oil additive constituents, that are present in many exhaust sources.

### **Catalyst Compatibility**

Automotive ceramic monolith have well designed pore structure (approx. 3-4 micron) that allow good chemical and mechanical bonding to the washcoat. The chemical components in the ceramic are immobilized, so little migration from the monolith into the catalyzed washcoat occurs.

Table 3.4 [31] lists a representative selection of currently available ceramic monolith geometries. An increase in cell density from 100 to 300 cpsi significantly increases the geometric area from 398 to 660 in<sup>2</sup>/in<sup>3</sup> (157 to 260 cm<sup>2</sup>/cm<sup>3</sup>) but decreases the channel diameter from 0.083 to 0.046 inches (0.21 to 0.12 cm). The wall of the ceramic drops in thickness from 0.017 to 0.012 inches (0.04 to 0.03 cm). The increase in cell density causes



an increase in pressure drop at a given flow rate. For example, a flow rate of 300 standard cubic feet per minute (SCFM) ( $8.4 \times 10^6$  cm<sup>3</sup>/min.) through a monolith of 1 ft<sup>2</sup> (929 cm<sup>2</sup>) by 1 inches thick (2.54 cm), the pressure drop for a 100 cpsi is about 0.1 inch (0.254 cm) of water, compared to about 0.3 inches for a 300 cpsi monolith.

Table 3.4 Physical properties of ceramic monolith [31].

<i>Cell Density (CPSI)</i>	<i>Hydraulic Channel Dia.(inches)</i>	<i>Open Frontal Area(%)</i>	<i>Geometric Surface Area(ft<sup>2</sup>/ft<sup>3</sup>)</i>	<i>Pressure Drop* (inches of water)</i>	<i>Wall Thickness (inches)</i>
64	0.099	70	340	0.075	0.019
100	0.083	69	398	0.095	0.017
200	0.059	72	576	0.210	0.012
300	0.046	65	660	0.300	0.012
400	0.044	71	852		0.006

\* Pressure drop for a 300 SCFM gas through a monolith, 12 x 12 x 1 inches

### 3.4.2 Metal Monoliths [31]

Monoliths made of high temperature resistant alumina-containing steels are becoming increasingly popular as catalyst supports, mainly because they can be prepared with thinner walls than a ceramic. This offers the potential for higher cell densities with lower pressure drop [34]. The wall thickness of a 400 cpsi metal substrate used for automotive applications is about 25 percent lower than its ceramic counterpart: 0.0015-0.002 inches (0.004-0.005 cm) compared to 0.006-0.008 inches (0.015-0.02 cm), respectively. The open frontal area of the metal is typically about 90 percent versus 70 percent for the ceramic with the same cell density. Its thermal conductivity is also considerably higher (by about 15-20 times) than the ceramic, resulting in faster heat-up. This property is particularly important for oxidizing hydrocarbons and carbon monoxide emissions when a vehicle is cold. Metals substrates also offer some advantages for converter installation in that they can be welded directly into the exhaust system. A common design is that of corrugated sheets of metal welded or wrapped together into a monolithic structure.

Adhesive of the oxide based washcoat to the metallic surface and corrosion of the steel in high-temperature steam environmental were early problem that prevented their widespread use in all but some specialized automotive applications. Surface pretreatment of the metal has reduced the adherence problems, and new corrosion-resistant steels are allowing metals to slowly penetrate the automotive markets. They are currently used extensively for low-temperature applications such as  $\text{NO}_x$  in power plants,  $\text{O}_3$  abatement

in airplanes, CO and VOC abatement and (quite recently) catalytic converters for natural gas fueled vehicles. They are usually about twice as expensive as their ceramics counterpart.

### 3.5 The concept of three-way catalyst system.

In the vicinity of the stoichiometric air/fuel ratios, the gas which is emitted from the engine contains small quantities of  $\text{NO}_x$ , CO, HC,  $\text{H}_2$  and  $\text{O}_2$ . A technique for feeding this gas through a catalyst, in order to reduce  $\text{NO}_x$  and to oxidize CO and HC, thereby decreasing the three components simultaneously by means of a single catalytic converter, has been employed in passenger cars. The catalyst used for this purpose is termed a three-way catalyst [25].

Such a simultaneous treatment of the three gas components requires that the concentrations of the respective constituents be maintained within a certain range, and that the reducing gases of CO,  $\text{H}_2$  and HC (for  $\text{NO}_x$ ) and the oxidizing gas of  $\text{O}_2$  (for CO and HC) exist in the quantities appropriate to their respective reactions. And thus, the range of air/fuel ratios satisfying these conditions is a very narrow  $\pm 0.25$ . When the air/fuel ratio deviates toward the rich side, the exhaust gas passing out of the converter contains more CO and HC and when the ratio deviates toward the lean side,  $\text{NO}_x$  increases. In an improved carburetor, the range of air/fuel ratios may be controlled to within a deviation of  $\pm 0.5$ , but such a range does not permit use of a three-way catalyst because more accurate control of the air/fuel ratio is required. To better cope with this situation, a technique has been

developed which detects the presence of  $O_2$  concentration in exhaust gas by means of a sensing device ( $O_2$  concentration detector), that uses the electric output obtained in order for a feedback type carburetor. Precious metals such as platinum, palladium, rhodium and ruthenium are used as the catalyst, to generate low levels of  $NH_3$ . A sufficiently durable  $O_2$  sensor, which is exposed to high temperature exhaust gases for a longtime, has not been devised. However, its durability has been improved considerably. And the  $O_2$  sensor is provided in some passenger cars. The three-way catalyst system of passenger cars employs EFI (Electronic Fuel Injection) or a feedback carburetor to control air/fuel precisely, and the complication of the catalysts system is unavoidable.

### 3.5.1 Oxygen Sensor.

The  $O_2$  sensor is designed to monitor  $O_2$  concentration in the exhaust gas and provide an electrical signal to the control unit. The  $O_2$  sensor is composed of a test-tube-like Zirconia element with platinum electrodes attached to both its surfaces [26]. The surface of the outer platinum electrode is coated with porous alumina to protect it physically. The Zirconia element is a kind of solid electrolyte, and generates an electrical potential according to the difference in  $O_2$  concentrations between both electrodes, when it becomes heated. In short, the  $O_2$  sensor is an oxygen concentration cell with the inside exposed to the ambient air and the outside to the exhaust gas.

The  $O_2$  sensor must be kept in the appropriate temperature range to ensure its effective operation and durability because the temperature of the



element has a great influence on the characteristics of the O<sub>2</sub> sensor such as sensor voltage, response time and internal resistance. In addition to these considerations, the location of the O<sub>2</sub> sensor must be determined carefully so that cylinder to cylinder deviation of the air-fuel ratio may be alleviated as much as possible. It is usually located on the converged room of the exhaust manifold. In the case of the liquefied petroleum gas (LPG) fueled engine, however, it must be attached close to the exhaust port to compensate for the lower exhaust gas temperature.

### **3.5.2 Air - to - fuel control system.**

Simultaneous oxidation and reduction can take place in a single catalytic bed, provided that the air to fuel ratio is adjusted precisely at the stoichiometric  $14.7 \pm 0.1$ . This precise metering is required for the three-way catalyst. A narrow "window" exists for some catalysts where more than 80 % conversion efficiency can be obtained on all three pollutants [35]. This precise metering cannot be attained by more than  $\pm 0.1$  from the set point ; a change of fuel type, a change in atmosphere humidity, and a change in altitude will also affect this ratio. A feedback control mechanism, equipped with an oxygen sensor to measure the oxygen pressure in the exhaust gas has been developed that can achieve this precision in the air/fuel ratio. This strategy also leads to good fuel economy and drivability. Thus, EFI system was proposed. EFI system has the highest potential for precise air-fuel ratio control. The concept of this operation is O<sub>2</sub> sensor monitoring the concentration of oxygen in the exhaust gas. Then the O<sub>2</sub> sensor sends the



signal through a circuit of operation. The controller determines the amount of injected fuel to be corrected.

### 3.5.3 Operating in the four windows.

There are many constraints in the design of a catalytic converter for an automobile. The desired converter volume is no more than the engine displacement and preferably half of that. The shape and location of converters are largely governed by whatever convenient space can be allocated in an exhaust automobile design, which means either a cylindrical object under the hood or a flat pancake or oval shaped object under the passenger seat [28]. The converter is asked to remove more than 90% of the inlet pollutants, at a space velocity of up to  $200,000 \text{ hr}^{-1}$ , or a contact time of 5 msec. after accounting for the volumetric expansion of gases with temperature. This gas hourly space velocity requires an extraordinarily fast catalyst, approaching in its activity that of the ammonia oxidation catalyst. On account of the dilute concentration of pollutants, the turnover number (defined as molecule of gas reacted per time per active site [36]) is seldom more than ten molecules per atom of platinum contained per second.

Another important constraint comes from the pressure drop across the catalytic bed, which must be kept to a minimum to avoid a loss in engine power and performance. This requirement is satisfied by a very shallow pellet bed of no more than ten pellets deep, a monolithic structure with many open parallel channels, or a pile of metallic screens and saddles.

every one of four variables : temperature , gas composition, gas flow rate and poison concentration. The catalytic system can tolerate occasional excursions from these windows, but prolonged excursions invariably lead to slow chronic ageing of quick failures as shown in Figure 3.5 [28].

In actual practice, an automobile is always in transient conditions: the catalyst is too cold during start-up and too hot during a long downhill cruise; the air/fuel ratio is too rich on idle and too lean while cruising; the exhaust gas flow is slow during idle, and fast during an upgrade cruise. The catalysts are also exposed to repeated cycles of heating and cooling, evaporation and condensation of water, pulsating flow from exhaust gases, vigorous shaking on the road, and a variety of poisons including lead and sulfur. The excursion from the optimal operating conditions cause the catalysts in automobiles to deteriorate prematurely [28].

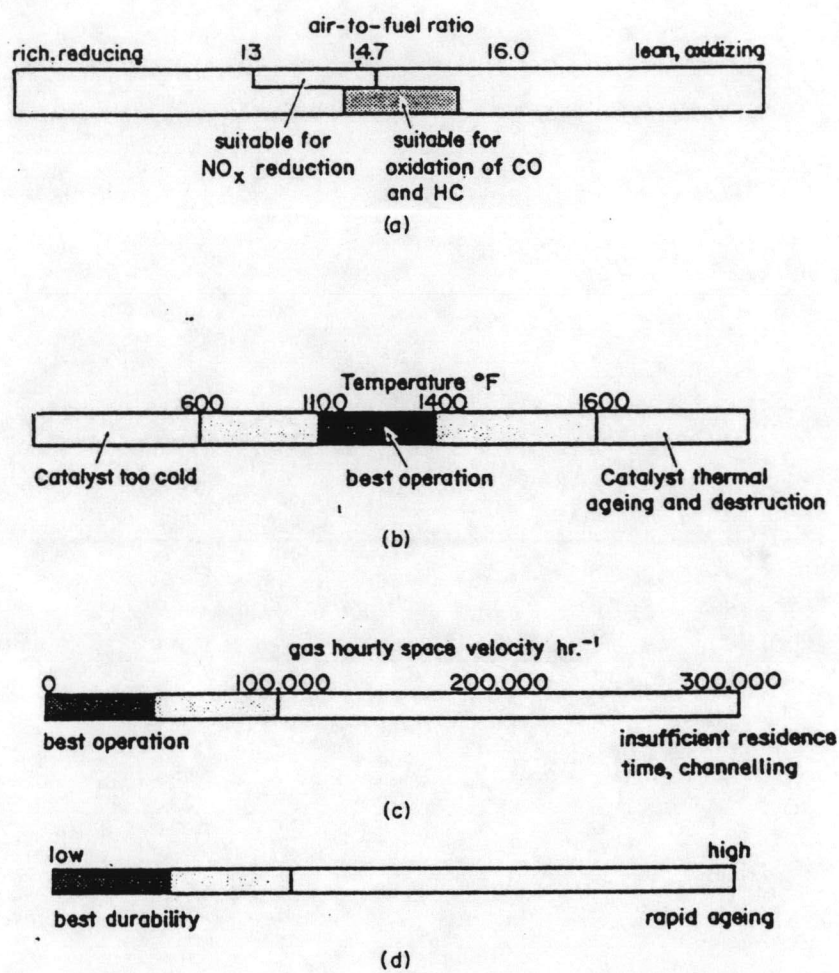


Figure 3.5 Four windows of operation [28]

Concurrent reducing and oxidizing is possible by controlling the air/fuel (A/F) ratio within a narrow band of  $\pm 0.3$  A/F ratio about stoichiometric A/F ratio, as shown in Figure 3.6 [26]. This narrow band in A/F ratio is very difficult to achieve with a conventional carburetor [28]. To achieve precise control of A/F ratio, computer control of fuel metering was employed. This computer controls fuel metering by responding to continuous sensing of oxygen in the exhaust gas as an indicator of A/F ratio in the engine.

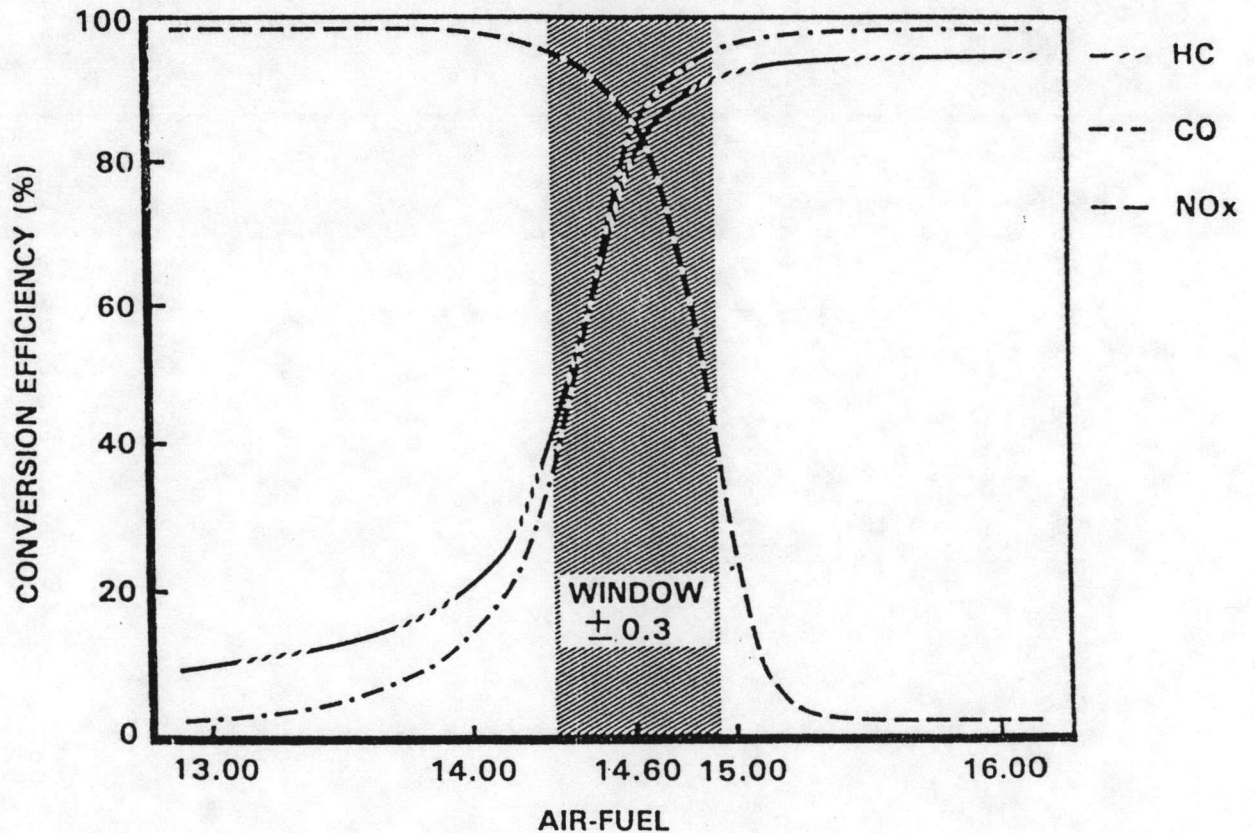


Figure 3.6 Conversion Efficiencies for a Typical Three-way Catalyst [26].