CHAPTER III

AUTOMOTIVE CATALYST

Air pollution, which has become a major social problem today, is caused by exhaust gas generated from boilers and incinerators (stationary sources), small-size incinerating equipments used for cooking in homes, restaurants, etc (miscellaneous sourced) as well as by emission from motor vehicles, air craft and ships (mobile sources). Motor vehicle emissions include exhaust emissions from the exhaust pipe, blow-by gas from the engine crankcase, fuel evaporative gas from the gasoline fuel tank and carburetor and particulaters from wear and tear of tire and brake.

Currently, emissions of three gaseous constituents in the exhaust from a vehicle are regulated. These constituents are unburned hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NO_x). Sources of automotive emission were shown in Figure 3.1[31]. For a typical vehicle, 20% of the unburned hydrocarbons was traced to vapors vented from the crankcase and 20% was traced to evaporation from two sources, the carburetor and the fuel tank. The engine exhausted the remaining 60% of the unburned hydrocarbons, as well as 100% of both carbon monoxide and oxides of nitrogen.

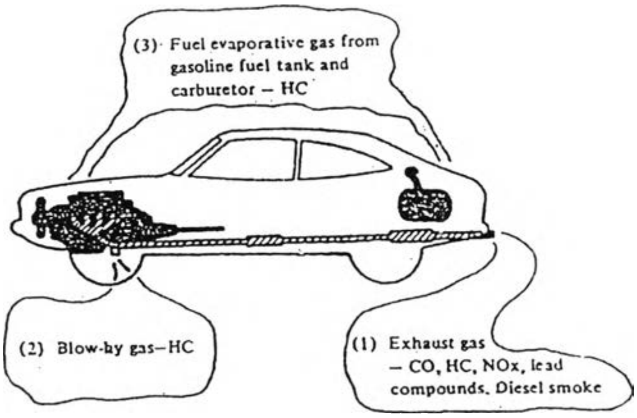

Figure 3.1 Sources of automotive emission

3.1 State of Air Pollution

3.1.1 Unburned 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 3.2 [32], 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 hydrocarbons result from excess fuel or fuel enrichment in the combustion chamber. This fuel enrichment is needed when the engine is cold so that enough volatile fuel is present in the cylinder to initiate combustion. An overall rich A/F produces high levels of HC [31].

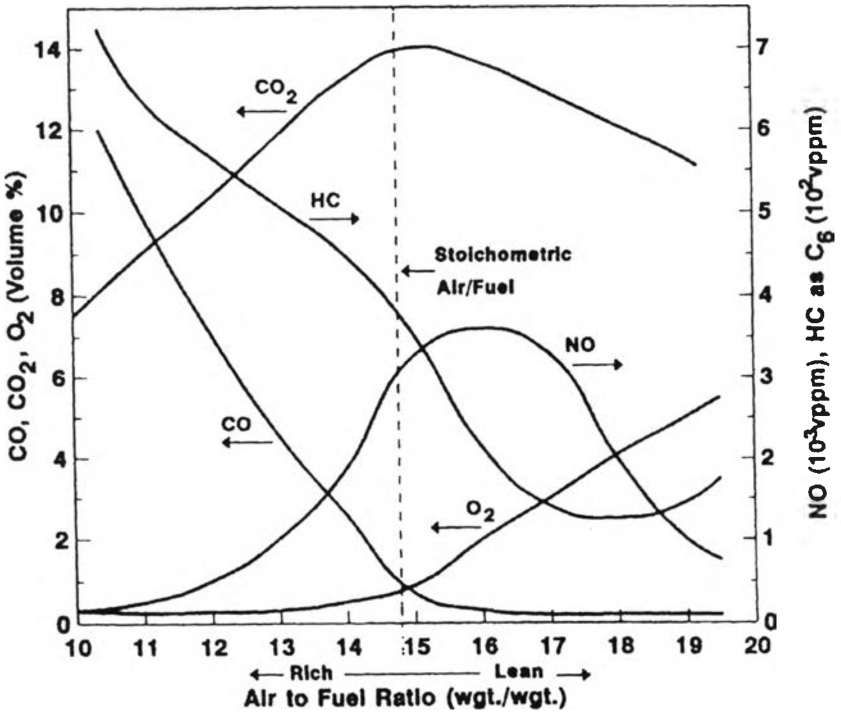

Figure 3.2 Spark-ignition gasoline engine emission as a function off air-to-fuel (A/F) ratio

3.1.2 Carbon monoxied (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 it is not much to known about chronic effect and because it contributes to the climate effect as its greenhouse potential is five times that of CO_2 [33]. As shown in Figure 3.2 [30] high concentrations of CO are discharged from an engine operating at rich A/F ratio (air/fuel). As A/F ratio approaches the stoichiometric to zero, but never quite drops to zero. 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_2.

As for CO resulting from 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.

3.1.3 Nitrogen oxides (NO_x)

Air pollution in the form nitrogen dioxide (NO_2) is understood to be originated from the oxidation of N_2 materials. Although the direct product of such combustion is mostly nitrogen monoxide (NO), this substance undergoes oxidization in the air to become NO_2. Sources of the emission of 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 [34]. 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 NO_x and 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.

NO_x output from an engine is also very sensitive to A/F ratio, as shown in Figure 3.2 [32], with the peak production occurring at an A/F ratio slightly lean from stoichiometric. NO production is associated with high temperatures, very little NO_x is produced during the cold start, in contrast to the large HC and CO outputs from a cold start.

3.2 Exhaust gas composition [35]

In an ideal case, and 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 on 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 pollution concentrations depend mainly on air-to fuel ratios, as shown in Figure 3.2 [32].

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:

$$\text{exhaust emission quantity} = (\text{exhaust emission concentration}) \times (\text{exhaust gas flow rate}) \times (\text{driving time})$$

The concentration respective emissions and the exhaust gas flow rate during the above four kinds of driving modes vary generally as shown the Table 3.1 [33].

Table 3.1 Exhaust emission concentration and exhaust gas flow rate at each driving mode [33]

Driving Modes	**Emission Concentration**	**Exhaust Gas Flow Rate**
Idling	CO and HC are high, and NO_x is low	Low
Acceleration (car starting or passing)	CO , HC and NO_x are high	High
Constant speed	CO and HC are low, and NO_x becomes higher at a higher speed	High at a higher speed
Deceleration	CO and HC, especially HC.are high,and NO_x 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 [33]. 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 [36]. 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 [36].

Table 3.2 The composition of exhaust gas emitted on the mixture in the vicinity of stoichiometrical air/fuel ratio is burnt [36]

Name of material	Volume rate (% or ppm)
N_2	83.5 (%)
O_2 (including argon)	2.22 (%)
CO_2	13.0 (%)
H_2	0.23 (%)
CO	0.97 (%)
HC	205 (ppm)
NO	2900 (ppm)
NO_2	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 [37] as follows:

Table 3.3 Typical Exhaust Gas Composition Spark Ignition Engine 1:8 [37]

Operation Conditions	Idling	Partial load	Full load
Torque (Nm)	0	26	114
Torque (%)	0	23	100
Rotational speed (min^{-1})	900	3,000	5,000
Temperature (°C)	280	505	910
Space velocity (Nl/l/h)	5,670	27,100	123,950
Linear velocity (m/s)	0.54	3.6	25.2
Residence time (s)	0.3	0.045	0.006
O_2 (Vol%)	1.17	0.8	0.43
NO_x (Vol-ppm)	162	1,850	2,670
HC (Vol-ppm)	689	514	380
CO (Vol%)	0.76	0.68	1.05
H_2 (Vol%)	0.25	0.22	0.35
SO_2 (ppm)	6.4	6.4	6.4
CO_2 (Vol%)	14.1	14.7	14.6

Residual : Nitrogen, water, and vapor

3.3 Catalytic reaction for pollution abatement [38]

The basic operation of catalyst is to perform the following reactions in the exhaust of the automobile [38]:

Oxidation of CO and HC to CO_2 and H_2O

$$C_xH_y + (1+y/4)O_2 \longrightarrow xCO_2 + (y/2)H_2O \qquad (3.1)$$

$$CO + 1/2O_2 \longrightarrow CO_2 \qquad (3.2)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (3.3)$$

Reaction of NO/NO_2 to N_2

$$NO\ (\text{or } NO_2) + CO \longrightarrow 1/2N_2 + CO_2 \tag{3.4}$$

$$NO\ (\text{or } NO_2) + H_2 \longrightarrow 1/2N_2 + H_2O \tag{3.5}$$

$$(2 + y/2)NO\ (\text{or } NO_2) + C_xH_y \longrightarrow (1 + y/4)N_2 + xCO_2 + y/2H_2O \tag{3.6}$$

The underbody location of the catalytic converter in the automobile is shown pictorially in Figure 3.3 [39]. 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 initial 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_x 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.

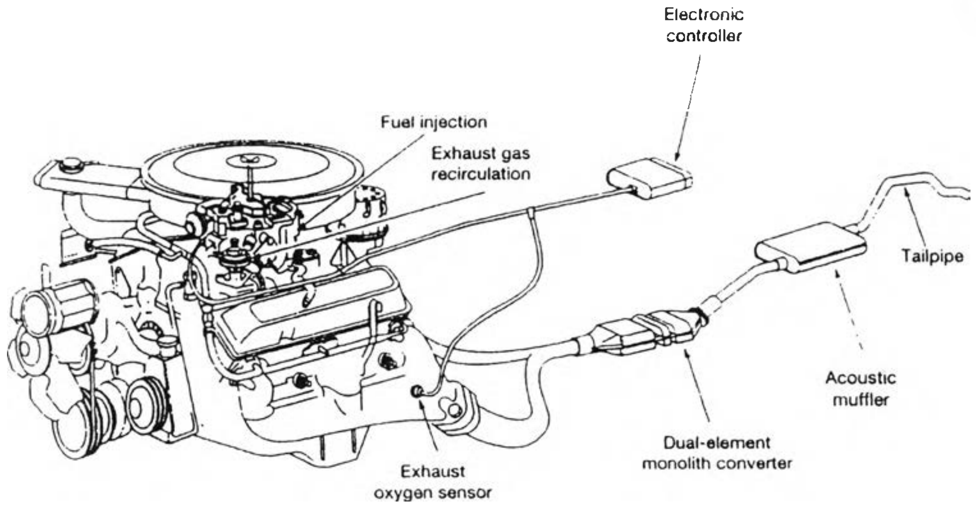

Figure 3.3 Location of a catalyst in underbody of an automobile [39]

3.4 Inside of the three-way catalytic converter [2]

There are five major components:

1. The substrate ;
2. The support ;
3. The stabilisers ;
4. The promoters ;
5. The platinum group metals.

3.4.1 The substrate

For the substrate of converter are shaped into spheroids, cylinders, monolithic honeycombs [40], and metallic mesh or saddles. A typical monolith converter is made by extruding cordierite into structure containing many parallel passages of square cross section. The monolithic supports are made of alumina and related materials such as cordierite ($Al_4Mg_2Si_5O_{18}$), mulite ($(3Al_2O_32SiO_2)_2$), spodument [$LiAl(SiO_3)_2$], and asbestos [$Mg_3(Si_2O_5)_2(OH)_2$]. They are chosen for their resistance to high temperatures and thermal stresses from repeated thermal cycling, and for their good mechanical strength in withstanding physical shock and vibrations.

The ceramic monoliths are usually cylinders from 3 to 6 in. in diameter, and 2 to 9 in. in length. They contain many parallel channels, and are sometimes surrounded by an integral outer skin. A corning monolith extruded and then fired, forming channels with square cross sections. An American Lava monolith is made with a corrugated paper processing machine, using a mixture of fiber and ceramics, and laying down horizontal and sinusoidal layers alternately. These two types of monoliths having walls ranging form 0.008 to 0.010 in. in thickness, so that the open space in the monolith amounts to 60 to 80%. The Dupont Torvex has hexagonal cells with diameters 1/8 to 3/8 in., with wall thickness from 0.03 to 0.05 in. There are other designs which contain much less open space, where the cross section is a plane penetrated with numerous circular holes arranged in geometric order. The designs with thick walls have the disadvantage of less open area and higher pressure drops, as well as a longer diffusion path for reactant molecules and a higher heat capacity.

3.4.2 The support

The support materials for the active ingredients must have high thermal stability, high resistance to attrition and crushing, low volumetric shrinkage with temperature, high surface area, and relatively low density and heat capacity. The most important material is probably gamma alumina (γ-alumina). The demand for rapid warm-up for automobile emission control has led to the development of high surface area materials of much lower densities, such as alumina substrates at 0.3 g/ml bulk density. The BET surface area of a pellet should be in excess of 100 m^2/g. While most substrates experience loss of surface area at temperatures exceeding 815°C, some stabilized aluminas have been developed that can tolerate occasional excursions of temperature exceeding 1100°C.

A high surface area alumina is usually place over the ceramic surface as "washcoat" with a thickness of about 0.001 in., which then acts as a substrate for the active ingredients.

3.4.3 The stabilisers

Stabilisers are often added to the washcoat to maintain the high surface area at the elevated temperatures which are encountered under operating conditions.

3.4.4 The promoters

Promoters are included to improve the activity or selectivity of the catalyst and can have a strong influence on performance. The most widely applied promoters in three-way catalysts are nickel and cerium.

3.4.5 The platinum group metals

The most successful class of active ingredient for both oxidation and reduction is that of the noble metals: silver, gold. ruthenium, rhodium, palladium, osmium, iridium, and platinum. Platinum and palladium readily oxidize carbon monoxide, all the hydrocarbon except methane, and the partially oxygenated organic compounds such as aldehydes and alcohols. Under reducing conditions, platinum can convert NO to N_2 and to NH_3.

The requirement for platinum, palladium and rhodium in autocatalyst is determined principally by the reactions that the metals are presented to catalyst:

$$HC \longrightarrow H_2O + CO_2 \tag{3.7}$$

$$CO \longrightarrow CO_2 \tag{3.8}$$

$$NO_x \longrightarrow N_2 + H_2O \tag{3.9}$$

In the early days of autocatalyst the principal requirement was to oxidize unburned hydrocarbon (HC), and carbon monoxide (CO). To do this catalysts of platinum, palladium, or a mixture of these two elements, were chosen. As legislation has become stricter and has focussed on additionally removing nitrogen oxides (NO_x) the role of rhodium to catalyst the reduction of NO_x to nitrogen and water has become critical.

The sources of platinum group metals (PGM) in the world that are suitable for economic exploitation are few. The principal sources is the Bushveld ligneous Complex in South Africa. Other significant mining for PGM occurs in the USSR, Canada and the USA. China is believed to produce same PGM but is still a net importer of the metals. Small amounts of PGM are also recovered elsewhere in the world either as placer deposits or as by products of base-metal mining, but the contribution of these to world supplies is insignificant. Table 3.4 indicates, the proven reserves of platinum, palladium and rhodium in South Africa, the USSR, Canada and the USA are considerable and sufficient to last for between 250 and 400 years at current rates of consumption.

Table 3.4 Reserves of platinum, palladium and rhodium (million oz) [34]

Origin	Pt	Pd	Rh
SOUTH AFRICA			
Merensky	333	141	17
UG2	437	365	83
Platreef	160	175	12
CANADA, Subdury	3	4	1
URSS, Noril'sk	50	142	6
USA, Stillwater	7	23	3
	990	850	120

3.5 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 NO_x, CO, HC, H_2 and O_2. A technique for feeding this gas through a catalyst, in order to reduce 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 [31].

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, H_2 and HC (for NO_x) and the oxidizing gas of O_2 (for CO and HC) exist in the quantities appropriate to their respective reaction. And thus, the range of air/fuel ratios satisfying these condition is a very narrow ± 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, NO_x increases. In an improved carburetor, the range of air/fuel ratios may be controlled to within a deviation of ± 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 deviced. 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 [33]. 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_2 sensor such as sensor voltage, response time and internal resistance. In addition to these considerations, the location of the O_2 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 ±0.1. This precise metering is required for the three-way catalyst. A narrow "window" exists for some catalyst where more than 80% conversion efficiency can be obtained on all three pollutants [41]. This precise metering cannot be attained by more than ± 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 derivability. Thus, EFI system was proposed. EFI system has the highest potential for precise air-fuel ratio control. The concept of this operation is O_2 sensor monitoring the concentration of oxygen in the exhaust gas. Then the O_2 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 [35]. The converter is asked to remove more than 90% of the inlet pollutants, at a space velocity of up to 200,000 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 [42]) 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 the 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 aging or quick failures as shown in Figure 3.4 [35].

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 and 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 [35].

Concurrent reducing and oxidizing is possible by controlling the air/fuel (A/F) ratio within a narrow band of ± 0.3 A/F ratio about stoichiometric A/F ratio, as shown in Figure 3.5 [33]. This narrow band in A/F ratio is very difficult to achieve with a conventional carburetor [35]. 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.

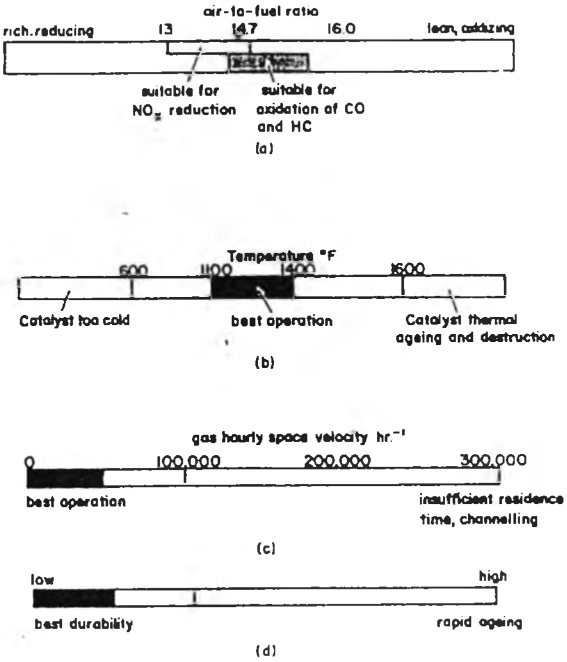

Figure 3.4 Four windows of operation [35]

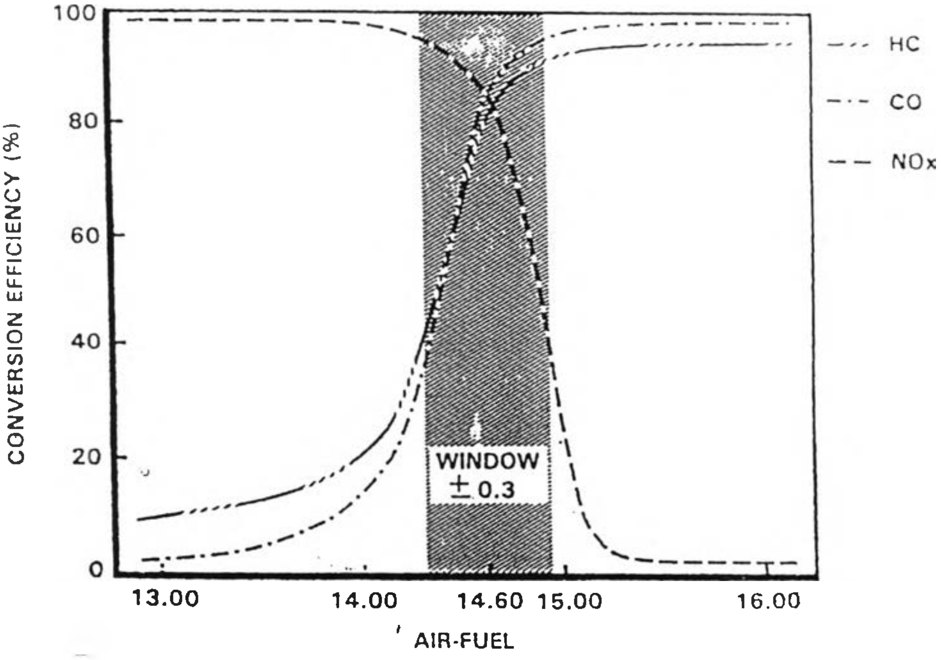

Figure 3.5 Conversion efficiencies for a typical three-way catalyst [33]