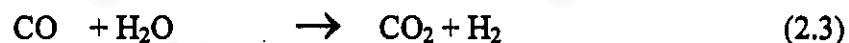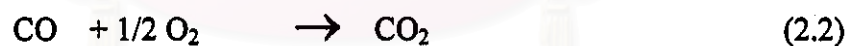# CHAPTER II

HONEYCOMB SUPPORT

For pollution abatement applications, it is common to utilize a honeycomb-supported catalyst to minimize the pressure drop associated with high flow rates. The honeycomb is usually installed inside a steel housing and physically fixed in the exhaust gas system. This allows the process effluent gases to pass uniformly through the channels of the honeycomb. The incoming pollutant-laden stream is often hot from the upstream process or, via a burner in the process line or a heat exchanger. In some caseË, it may have to be preheated to a temperature sufficient to initiate and maintain the catalytic reactions [1].
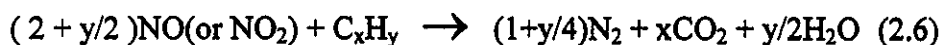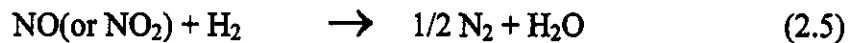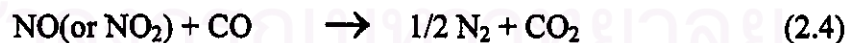
2.1 The catalytic reaction for pollution abatement

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

Oxidation of CO and HC to CO$_2$ and H$_2$O

$$C_xH_y + (1 + y/2)O_2 \rightarrow xCO_2 + y/2H_2O \qquad (2.1)$$
$$CO + 1/2\,O_2 \rightarrow CO_2 \qquad (2.2)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2.3)$$

Reduction of NO/NO$_2$ to N$_2$

$$NO(\text{or } NO_2) + CO \rightarrow 1/2\,N_2 + CO_2 \qquad (2.4)$$
$$NO(\text{or } NO_2) + H_2 \rightarrow 1/2\,N_2 + H_2O \qquad (2.5)$$
$$(2 + y/2)NO(\text{or } NO_2) + C_xH_y \rightarrow (1+y/4)N_2 + xCO_2 + y/2H_2O \qquad (2.6)$$

The underbody location of the catalytic converter in the automobile is shown pictorially in figure 2.1. When a driver first starts the automobiles, both the engine and catalyst are cold. As the exhaust gradually warms, the converter temperature 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 fast, 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 [1].
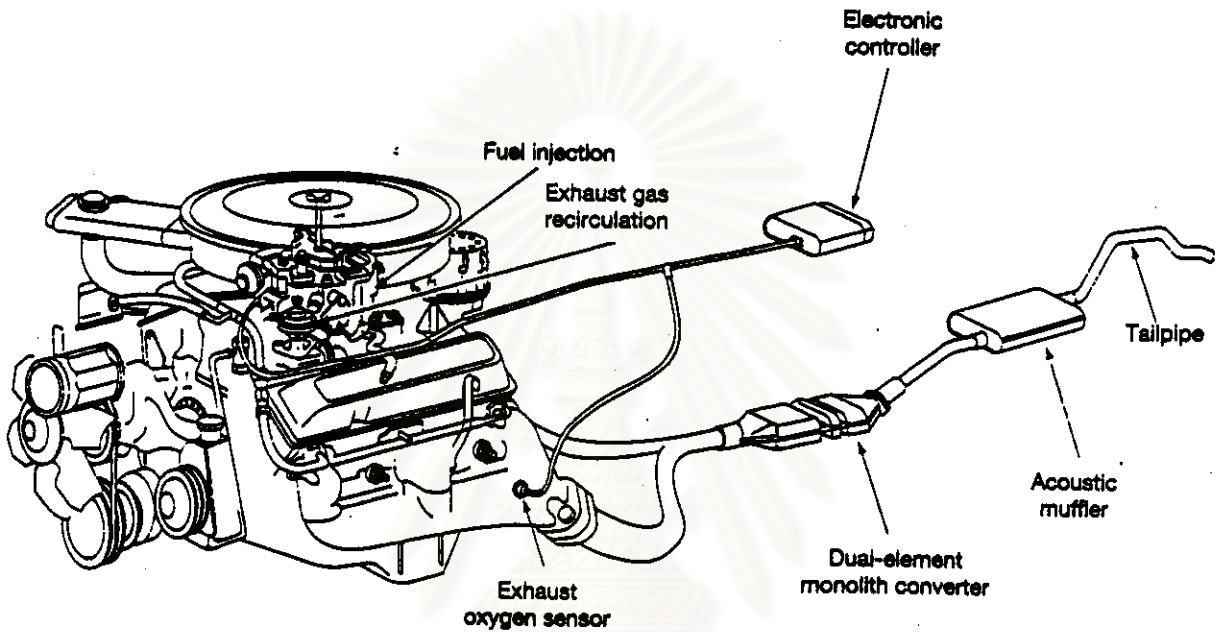

Figure 2.1 Location of a catalyst in underbody of an automobile [1]

2.2 Substrate systems

The catalytic converter (or more correctly the catalytic exhaust converter) consists of metal housing, a substrate and the actual active catalytic layer.

In turn, there are three different substrate systems:

- pellets
- ceramic monoliths
- metallic monoliths

2.2.1 Pellets

The pellet type of substrate was firstly introduced in the US and Japan. Pellets have functional deficiencies of nonreproducibility in packing pattern and changes in packing pattern during use. They wear at the surface where the catalyst is located , and therefore, require catalyst coatings diluted with ingredients that impart resistance to spalling and abrasion. The surface near the contact between pellets is poorly exposed and of minimum catalytic effectiveness. Small pellets with high pressure drop characteristics must be used to obtain higher surface area. The high pressure drop requires a thin bed design which leads to sharp temperature gradients within the bed and too low linear flow velocities for the resulting large frontal area. Dense material must be used for abrasion and crush resistance. The increased mass produces high heat capacity and sluggishness in response to heat. Pellets form relatively small flow channels with high macrotortuosity, which results in plugging and nonuniform flow patterns. A principal virtue of pellets is a relatively low selling price [3].
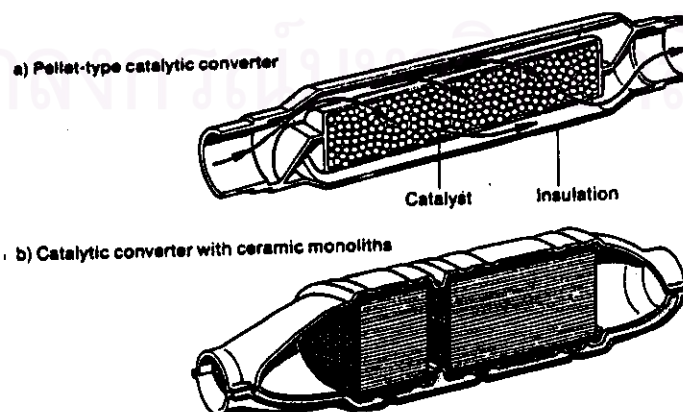

Figure 2.2 Substrate systems [3].

2.2.2 Monolith

Monolithic or honeycomb materials offer a number of advantages over more traditional pellet-shapes catalyst and, thus, are now widely used as support in environmental applications. It is a unitary structure composed of inorganic oxides of which may be square, sinusoidal, triangular, hexagonal, round, and so on. Five types of monolithic honeycombs are shown in figure 2.3 [1]. A triangular channels is shown in figure 2.3a, whereas a layered honeycomb steel structure with hexagonal shaped channels is shown in figure 2.3b. A square-channels extruded ceramic with 400 cells per square inch (the most commonly used for automotive applications) is shown in figure 2.3c. A layered steel structure, also with sinusoidal channels, is shown in figure 2.3d and a metallic monolith wound in a S-shape, with sinusoidal channels, is shown in figure 2.3e.

Commercial ceramic monoliths have large pores and low surface areas (i.e., 0.3 m^2/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 materials such as Al_2O_3 which will be subsequently impreganated with a catalytic component such as Pt. This refered to as the *catalyzed washcoat*, illustrated in figure 2.4. The washcoat can be seen deposited over the entire wall. The thickness of the washcoat depends primarily on the geometry of the channel and the coating method. The pollutant-containing gases enter the channels uniformly and diffuse to the catalytic sites where they are converted catalytically to harmless products.

Monoliths offer a number of design advantages that have led to their wide-spread use in environmental apllications such as catalytic converter used for automotive emissions control. However, the most important advantage 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, compactness, freedom in reactor orientation, and so on.

Monoliths are generally fabricated from ceramic or metal. The characteristics and properties of both types of monolith are described below:
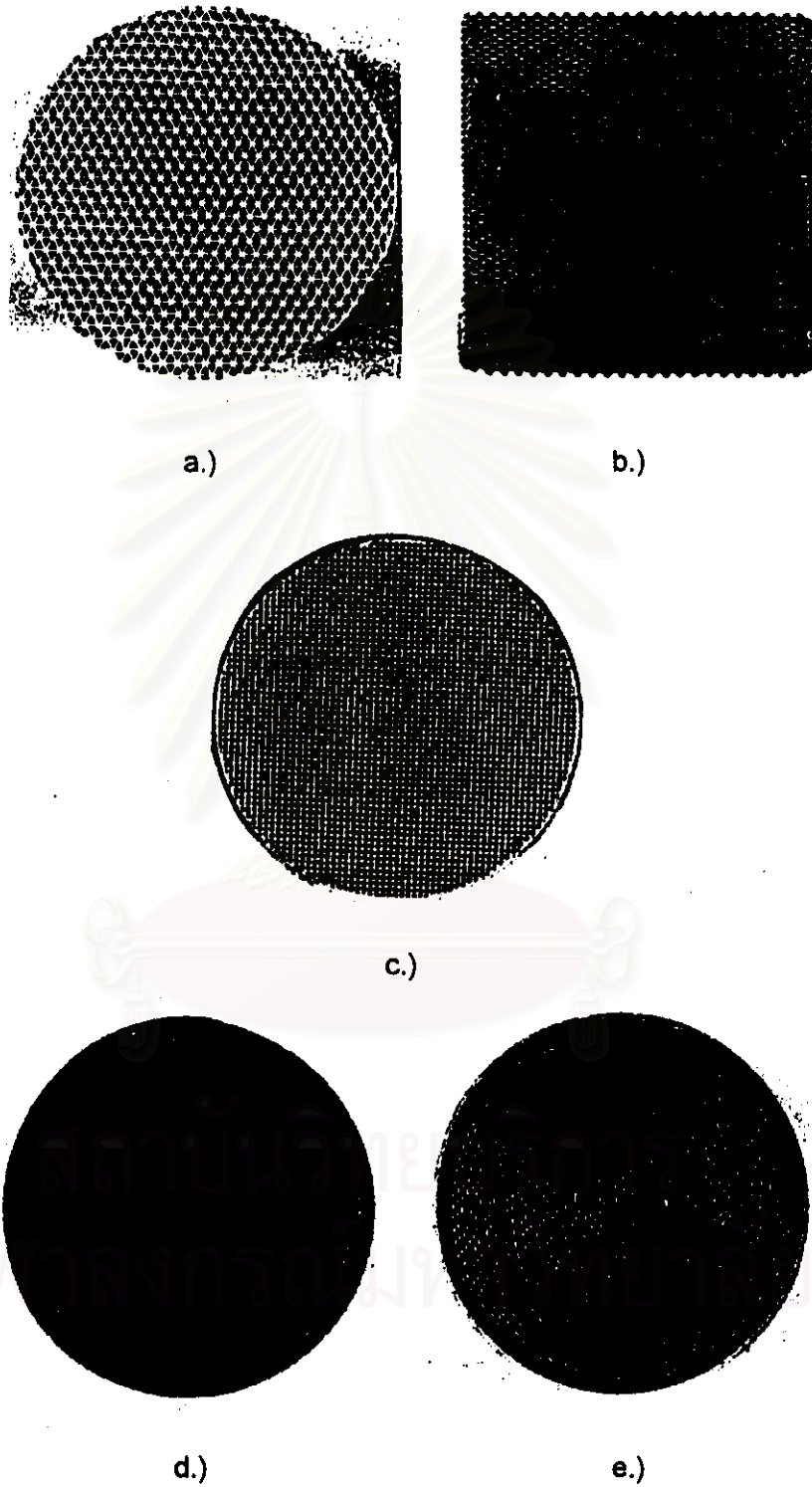
Figure 2.3 Some examples of monolithic support cross section [1].
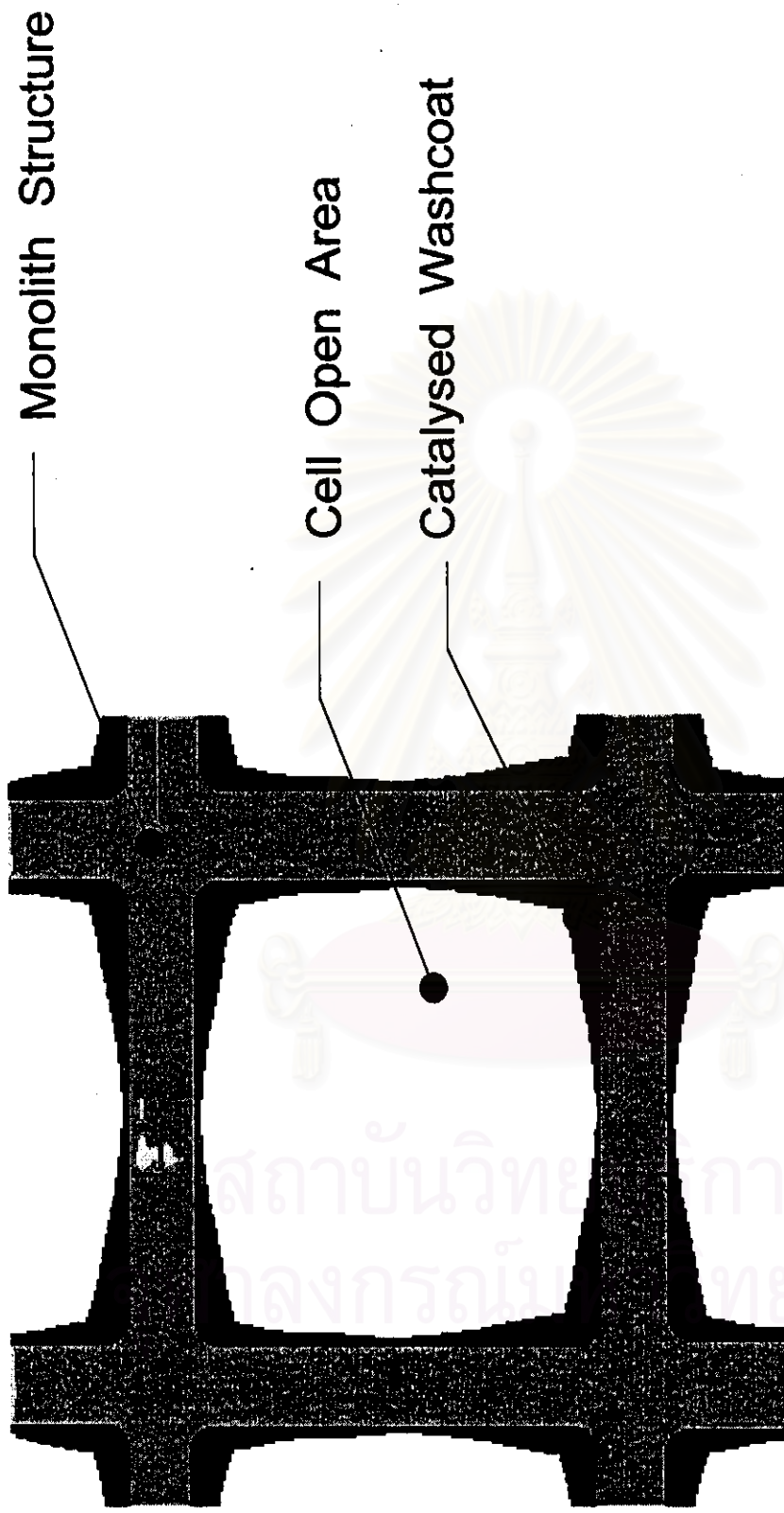
Figure 2.4 Ceramic monolith coated with a catalyzed washcoat.

2.2.2.1 Ceramic Monoliths [1]

The monolithic supports are made of alumina and related materials such as cordierite ($Al_4Mg_2Si_5O_{18}$), mullite ($(3Al_2O_3 2SiO_2)_2$), spoumene ($LiAl(SiO_3)_2$), and asbestos ($Mg_3(Si_2O_5)_2(OH_2)$) .

Synthetic cordierite, the first mentioned above, is by far the most commonly used ceramic for monolithic catalyst support applications. Raw materials such as kaolin, talc, alumium hydroxide, and silica are blended into a paste and extruded and calcined. It is possible to produce sizes up to about 27.94 cm in diameter and 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.

Cordierite monolith posses several important properties that make this materials preferable for use as a support. These properties are described below.

Thermal Shock Resistance

By nature of its low thermal expansion coefficient ($10 \times 10^{-7}/°C$), 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 approximately over 210 kilograms per square centimeter. 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 strongly immobilized, so little migration from the monolith into the catalyzed washcoat occurs.

Table 2.1 lists a representative selection of currently available ceramic monolith geometries. An increase in cell density from 100 to 300 cpsi (cell per square inch) significantly increase the geometric area from 157 to 260 cm^2/cm^3 but decrease the channel diameter from 0.21 to 0.12 cm. The wall of the ceramic drops in thickness from 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 x 10^6 cm^3/min.) through a monolith of 929 cm^2 by 2.54 cm thick, the pressure drop for a 100 cpsi is about 0.254 cm of water, compared to about 0.762 cm. of water for a 300 cpsi monolith.

Table 2.1 Physical properties of ceramic monolith [1].

Cell Density (CPSI)	Hydraulic Channel Dia. (inches)	Open Frontal Area(%)	Geometric Surface Area(ft^2/ft^3)	Pressure Drop(inches of water)	Wall Thickness (inches)
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	no data	0.006

2.2.2.2 Metal Monoliths [1]

Monoliths made of high temperature resistant alumina-containing steels are catalyst supports which have found several applications, mainly because they can be prepared with thinner walls than a ceramic. This offers the potential for higher cell densities with lower pressure drop. The wall thickness of a 400 cpsi metal substrate used for automotive applications is only about 25 percent of its ceramic couterpart: 0.004-0.005 cm compared to 0.015-0.02 cm, respectively. The open frontal area of the metal is typically about 90 percent versus 70 present 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. Metal 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 NO_x in power plants, 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.