CHAPTER III

THEORY

A chemical reaction and multistage distillation can be carried out simultaneously. The combined unit operation, called reactive distillation, especially suits those chemical reactions where reaction equilibrium limits the conversion in a conventional reactor to a low-to-moderate level. By continuously separating products from reactants while the reaction is in progress, the reaction can proceed to much higher level of conversion than otherwise possible.

The concept of reactive distillation is not new. The technique was first applied in the 1920's to esterification processes using homogeneous catalysts and was reviewed by Keyes in 1932. Implementation of the reactive distillation for reactions that rely on a solid heterogeneous catalyst is a more recent development.

In this chapter, the basic knowledge on the reactive distillation configurations and advantages of reactive distillation are described. Finally, some information on a solid heterogeneous catalyst, Beta zeolite, is provided.

3.1 The reactive distillation configurations

A conventional configuration for a process involving a catalytic chemical reaction with a solid catalyst involves two steps of chemical reaction and subsequent separation. In the chemical reaction step, reactants are brought into contact with solid catalysts at appropriate process conditions in one or more reactors. The stream leaving the reactor section then goes to one or more separation steps where unconverted reactants are separated from the products of the reaction and the inerts. The unconverted reactants, in some cases, may be recycled to the reaction section. When a substantial amount of inerts are present in the system, at least two separation units for

separation of high purity product and for separation of the unconverted reactants from the inerts are required. The separation process typically chosen is distillation.

A conventional process configuration is shown in Figure 3.1. The separation process is distillation. In the case, a reaction product is less volatile than reactants and inerts. The flow diagram of the application of reactive distillation to this process is shown in Figure 3.2. The middle section of the column is the reactive distillation section. For a non-azeotopic chemical system, separation of the inerts takes place in the rectification section of the column and the purification of the product takes place in the stripping section.
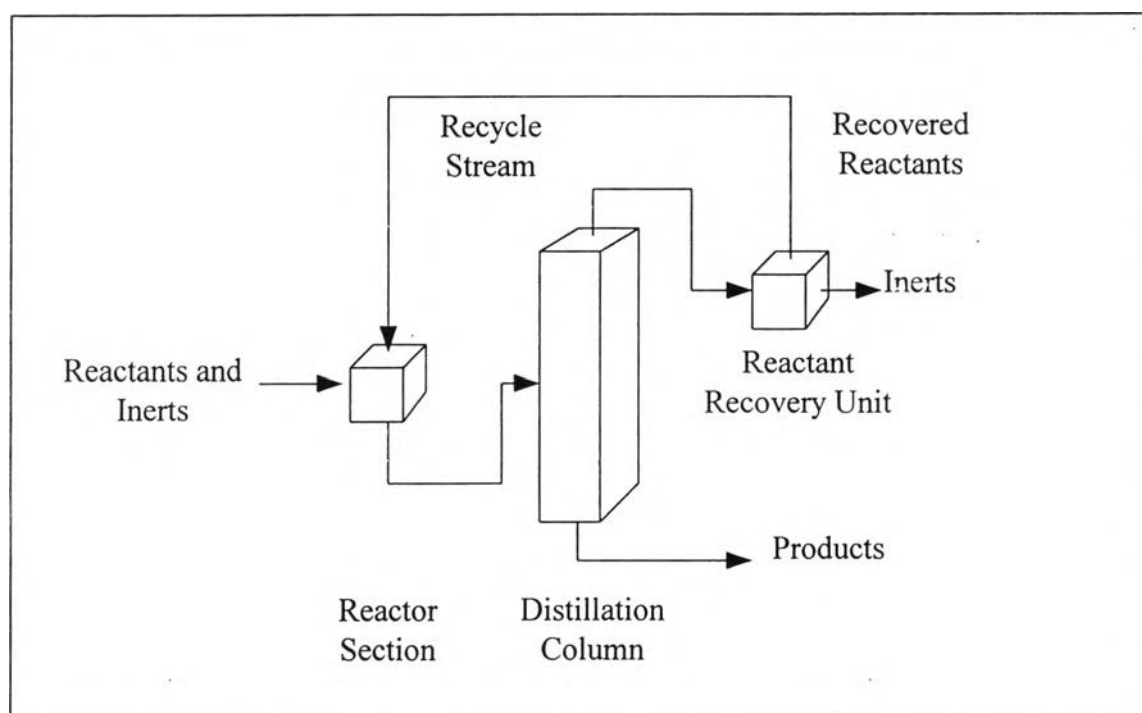

Figure 3.1 Conventional process involving reaction followed by separation.
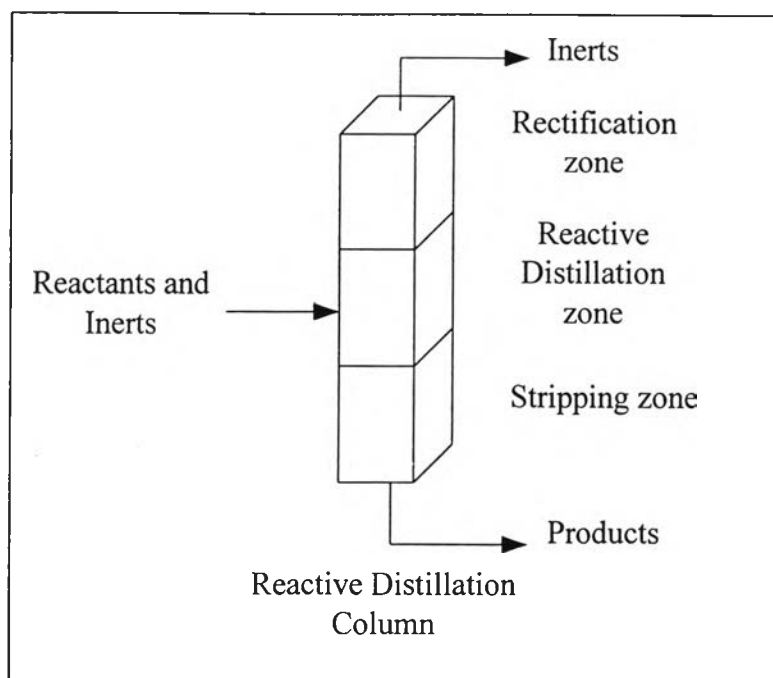
Figure 3.2 Reactive distillation applied to the same process.

In the presence of a solid catalyst bed, the reactive distillation can be carried out in several different configurations. In one configuration, the solid-catalyzed chemical reaction and the multistage distillation occur simultaneously in a continuum - that is, there is spatial continuity along the length of the column. Both reaction and distillation take place in every thin horizontal slice of the reactive distillation section of the column.

In the other configuration, the reaction and distillation proceed in alternating steps. Here, the reactive distillation section of a column contains both the catalyst contact device and the distillation device. A reaction occurs in the catalyst contact device and then the reacting phase passes to the distillation device for vapor/liquid contact and separation. These two steps occur alternately. By making the steps of infinitely small size, this configuration becomes equivalent to the first one.

In both configurations, a rectification section may be located above the reactive distillation section of the column and a stripping section may be located below it, depending upon purity specifications.

In some systems a combination, as shown in Figure 3.3, of the conventional process and reactive distillation may be optimal. Since part of the conversion is shifted to the reactive distillation column, the size of the fixed-bed reactor becomes smaller than in the conventional process, or the number of reactors may be decreased. The reactor effluent is the reactive distillation column feed and the remaining conversion takes place in the reactive distillation zone.
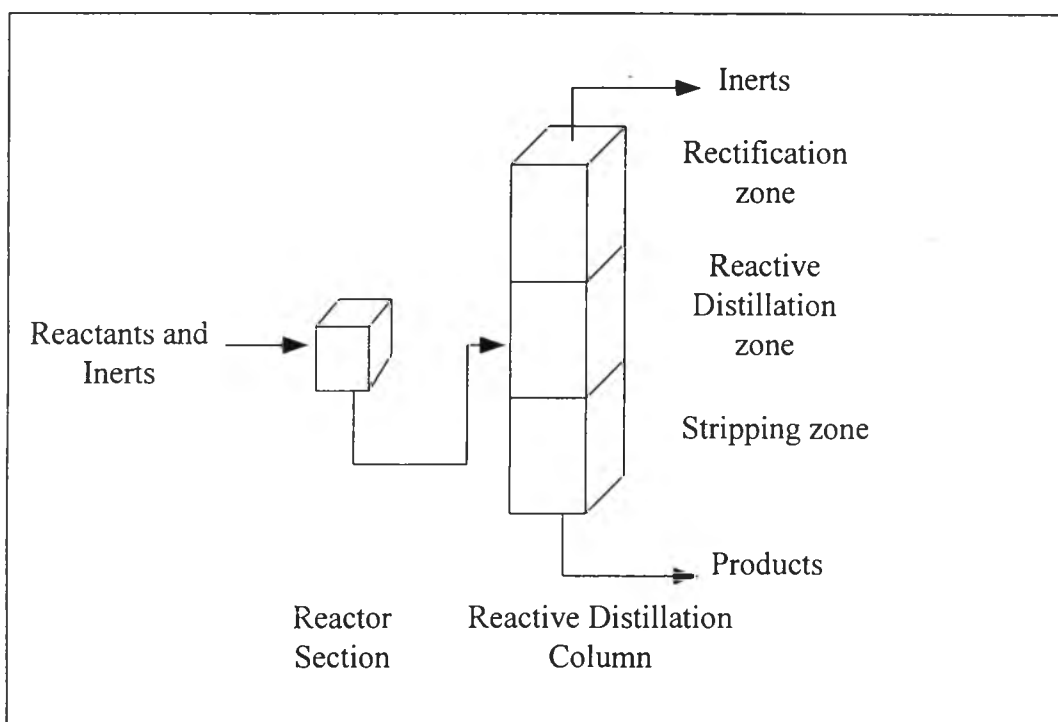

Figure 3.3 Combining reactive distillation with a conventional process offers benefits.

As shown in Figures 3.2 and 3.3, the external reactant-recycle sites can be eliminated under certain conditions with reactive distillation. External recycle of

reactants is eliminated for non-azeotopic chemical systems if the reactants in the fresh feed are present in stoichiometric proportion and the conversion in the reactive distillation section of the column is very high so that the concentration of all unconverted reactants in the distillate product is very low.

3.2 Advantages of reactive distillation

Application of reactive distillation to a catalytic chemical reaction using solid catalysts, as shown in Figure 3.2 and 3.3, leads to a substantial cost savings compared to a conventional process. These savings result from:

• Lower capital costs due to less equipment: reaction and separation are carried in the same column, this eliminates one process step with associated major equipment, pump, piping, and instrumentation. For reactions with high heat of reaction, the need for interstage heat transfer equipment is eliminated. All heat transfer takes place at the reboiler and condenser.

• Lower operating costs due to higher conversion per pass. This leads to a higher rate of production, plus the unconverted reactant concentration may be low enough to eliminate recycling. The cost per unit mass of product is less. If the reaction is exothermic. The heat of reaction is utilized for the distillation and results in energy saving.

However, the most important benefit of reactive distillation is a reduction in capital investment. By carrying out the chemical reaction and distillation in the same vessel, one process step is eliminated, along with the associated pumps, piping, and instrumental.

Other benefits depend on the specific chemical reaction. Chemical reactions that are characterized by unfavorable reaction equilibrium, high heat of reaction, and significant rate of reaction at distillation temperature are particularly good candidates for reactive distillation.

3.3 Effect of operating conditions on the performance of reactive distillation

Each chemical reaction has a reaction equilibrium. The chemical composition at equilibrium is such that the Gibbs free energy is minimum for a given temperature. There are some chemical reactions catalyzed by a solid catalyst for which, at a reasonable temperature, the fluid mixture at chemical reaction equilibrium still contains substantial concentrations of the unconverted reactants. Even if a high concentration of one or more of the reactants is present, the reaction may still not completely consume the stoichiometrically limiting reactant. Such reactions are generally described as equilibrium-limited reactions. For such chemical reactions, the conversion of the limiting reactant can be substantially increased by continuous removal of the products from the reacting mixture.

Some chemical reactions have significant heats of reaction (ΔH_f) that may be exothermic or endothermic. In an adiabatic reactor, this leads to a marked change in the temperature of the reaction mixture as the reaction progresses. This large temperature change will unfavorably shift the chemical equilibrium, lower the conversion, and potentially reduce selectivity. It may also detrimentally affect catalyst stability. For such chemical reactions in a conventional process, good design may mandate splitting the reactor up into several stages with interstage cooling for exothermic reaction or interstage heating for endothermic reactions. An alternative may involve providing heat-transfer area inside the reactor. In either case, the capital cost of the equilibrium goes up.

In a reactive distillation column, the heat of reaction does not affect the temperature and, hence, the reaction equilibrium. At any point near the catalyst, the heat of reaction causes additional mass transfer (vaporization or condensation) between the vapor and liquid phases, over and above and the mass transfer occurring for distillation alone (that is, without the reaction). The temperature of the phase where the reaction occurs will be the bubble (or dew) point temperature at its composition; it will be uniform and constant across the cross-section of the column. So, heat-transfer equilibrium to remove or supply the heat of reaction is obviated. In

the case of an exothermic reaction, the heat of reaction is utilized directly for the distillation. Those chemical reaction systems, that exhibit either unfavorable reaction equilibrium and significant heat of reaction can benefit the most from reactive distillation technology.

Reactive distillation is especially applicable to a certain class of reactions that employ solid catalysts. The important points that characterize such chemical/catalyst systems are the activity of the catalyst at distillation conditions and the relative volatility of the reactants and products. Proper balance between these two characteristic makes some chemical systems excellent candidates for use of the technique. A chemical/catalyst system in which the preferred temperature range of the catalyst either matches or substantially overlaps that for the distillation is an excellent candidate for reactive distillation.

The pressure, of course, must also be suitable. The range of pressure for distillation is selected to provide efficient separation of the unconverted reactants and the final products, based on a number of considerations. The available condenser coolant temperature generally sets the minimum possible column pressure, while the maximum column pressure is set by the available reboiler heating-medium temperature. Within the range, the pressure should be selected so as to optimize the process economics from both capital and operating cost standpoint. A higher column operating pressure generally reduces the relative volatility of the key components, which in turn increases the reflux ratio or number of theoretical stages required for a fixed degree of separation. At a fixed diameter, the vessel wall thickness increases with increasing pressure. On the other hand, at a fixed mass loading, higher column pressure decreases the column diameter because the vapor volumetric load decreases.

The pressure of the column and the operating temperature are related by the vapor/liquid equilibrium (VLE) of the chemical system. Other considerations may include the potential for degradation or polymerization of the chemical components at the operating temperature in the column.

Most catalytic reactions have a preferred range of temperature in which the catalyst can be used efficiently. In this range, the catalyst is thermally stable, and the rate of reaction and the selectivity to the desired product are high enough to make the operation economically viable. Thermal stability of the catalyst and selectivity for the desired product most likely sets the upper limit whereas the catalyst activity sets the lower limit. A chemical/catalyst system for which the distillation and reaction temperature ranges overlap is ideally suited for reactive distillation.

Besides temperature, other process parameters may affect the stability of the catalyst. For example, a minimum concentration of one of chemical components may be needed at the catalyst surface to prevent catalyst fouling. Ensuring that the reacting fluid phase meets this criteria may place additional constrains on the column pressure and temperature.

The number of solid catalyzed chemical reactions for which the reactive distillation is most beneficial is large. For many of these reactions, existing catalysts have good activity, selectivity, and stability in the temperature range suitable for distillation.

When evaluating the activity of a catalyst in the temperature range suitable for distillation, however, it is important to distinguish between the fixed-bed process and the reactive distillation process. Following the common practice of evaluating activity in a fixed-bed laboratory (pilot plant) can give misleading results because of the reactant equilibrium limitation inherent to a fixed-bed process. For a fixed temperature range, a catalyst may exhibit higher net reaction rate in a reactive distillation pilot plant than in a fixed-bed pilot reactor.

3.4 A solid heterogeneous catalyst : Beta zeolite

Beta zeolite is an old zeolite discovered before Mobil began the "ZSM" naming sequence. As the name implies, it was the second in an earlier sequence. Beta zeolite was initially synthesized by Wadlinger *et al.*(1995) using tetraethylammonium

hydroxide as an organic template. The structure of Beta zeolite was only recently determined because the structure is very complex and interest was not high until the material became important for some dewaxing operations. From studies of Treacy and Newsam, and Higgins et al. (1988) Beta zeolite is an intergrowth hybrid of two distinct but closely related structures that have tetragonal and monoclinic symmetry. In both systems, straight 12-membered ring channels are present in two crystallgraphic directions perpendicular to [001], while the 12-membered ring in the third direction, parallel to the c axis, is sinusoidal. The sinusoidal channels have circular openings (5.5 A°) and the straight channels have elliptical openings. The only difference between the two polymorphs is in the pore dimension of the straight channels. In tetragonal system, the straight channels have elliptical openings. In tetragonal system, the channels have openings of 6.0x7.3 A°, whereas in the monoclinic system they are 6.8x7.3 A°.

This zeolite may offer interesting opportunities as a catalyst, since it combines three important characteristics: large pores (12-membered oxygen ring), high silkica-to-alumina synthesis ratio and tridirectional network of pores. In addition, the dimensions of one type of pores (5.5 A°) can give a certain level of shape selectivity. This has been shown to apply to isomerization of C_4-C_7 hydrocarbons to gasoline fractions with increasing octane value, to transalkylation of xylenes, and to condensation of benzene and formaldehyde (Panichsarn *et al.*, 1999).

3.5 Catalyst support for the reactive distillation

The design of multifunctional reactors needed for the reactive distillation is difficult due to the conflicting demands of good distillation characteristics on the one hand, and good reactive distillation characteristics on the other. A compromise that is currently used, consists of distillation particles. Due to the size of the catalyst containers, the efficiency and selectivity of the catalyst material could be mounted in the column as a thin, rigid film on the type of structured column packing that is commonly used in distillation processes, or on comparable structures. The structure of the distillation packing then ensures good distillation characteristics, while the large

contact area between catalytic film and reaction mixture, combined with the short diffusion length, ensues a high overall efficiency and selectivity of the reaction.

At Delft University of technology, technology has been developed to prepare binderless films of catalytically active zeolite crystals on metal and ceramic supports. In short, the preparation procedure consists of immersing the support structure in an aqueous solution containing the reactants for zeolite synthesis, after which the system is heated and zeolite crystals grow on the surface of the support (Oudshoorn et al., 1999).

However, the commercial ceramic supports, ceramic monoliths, have large pores and low surface areas, 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 impregnated with a catalytic component such as Pt. This referred to as the catalyzed washcoat, illustrated in Figure 3.4. The washcoat depends primarily on the geometry of the channel and the coating method. The pollutant-containing gases enter the channels uniform 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 widespread use in environmental applications 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 channel offers less resistance to flow than that of pellet-type catalyst. Low pressure drop translates to lower compressor costs for stationary 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.
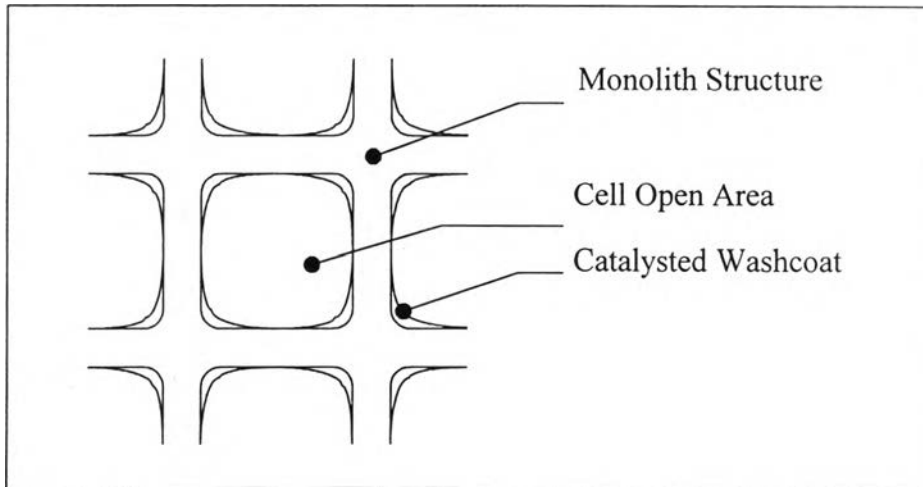
Figure 3.4 Ceramic monolith coated with a catalyzed washcoat.

Ceramic monolithic supports are made of alumina and related materials such as cordierite ($Al_4Mg_2Si_5O_{18}$), mullite ($3Al_2O_3SiO_2)_2$, spoumene ($LiAl(SiO_3)_2$), and asbestos ($Mg_3(Si_2O5)_2(OH)$).

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, aluminium 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 9 to 600 cells per square inch (cpsi). The conversion desired, the physical space available for the reactor, and engineering constraint 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 (10×10^{-7}/K), 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 expand 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 1,573 K far greater than temperature expected for modern environmental applications. The materials are also resistant to harsh environmental such as high temperature, stream, sulfur oxides, oil additive constituents, that are present in many exhaust sources.

Catalyst compatibility

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

Table 3.1 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) (8.4x106 $cm^3/min.$) 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 3.1 Physical properties of ceramic monolith.

cell density (cpsi)	Hydraulic Channel Dia. (inches)	Open frontal Area (%)	Geometry surface area (ft^2/ft^3)	Pressure Drop (inches of H_2O)	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	-	0.006

Metal supports, metal 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 ceramic with the same cell density. its thermal conductivity is also considerable higher (by about 15-20 times) than the ceramic, resulting in faster heat-up. This property is particurarly important for oxidizing hydrocarbons and carbon monoxide emissions when a vehicle is cold. Metal substrates also offer some

advantages for converter installations 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 used in all but some specialized automotive applications. Surface pretreatment of the metal has reduced the adherence problems, and new corrosion-resistant steel are allowing metal to slowly penetrae the automotive markets. They are currently used extensively for low-temperature aplications 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.