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Catalysis: A Look At The Basics

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Richard Carranza, Contributing Technical Editor

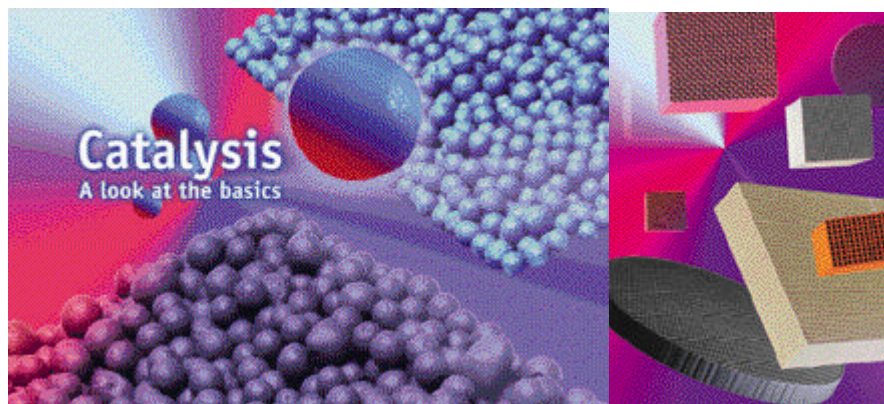
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In some applications, the catalysts are granular. The granular catalyst is fluidized in a gaseous system, such as a fluidized cracker. The catalyst can also be fluidized in a liquid system, such as a bubble column. But, in other applications the catalyst is fixed or placed on a support-that's the case with pellets, beads and monoliths.

The catalytic reaction process, or "catalysis" as it is called, enhances chemical reactions by reducing the amount of energy required to activate the reaction. Catalysis causes the reaction to occur at lower temperatures and higher rates than in noncatalytic processes.

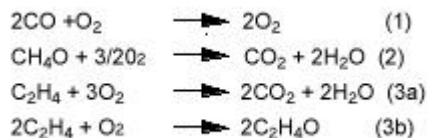
Take, for example, the combustion of light hydrocarbons without a catalyst. Noncatalytic methods require operating temperatures up to 1,800°F and residence times of 1 sec to achieve a 99% destruction efficiency. Catalytic combustion accelerates the reaction, causing it to occur at about 500°F with a 0.05-sec residence time. The advantages of catalysis include lower energy consumption, shorter residence time and smaller equipment.

The mechanisms of catalysis

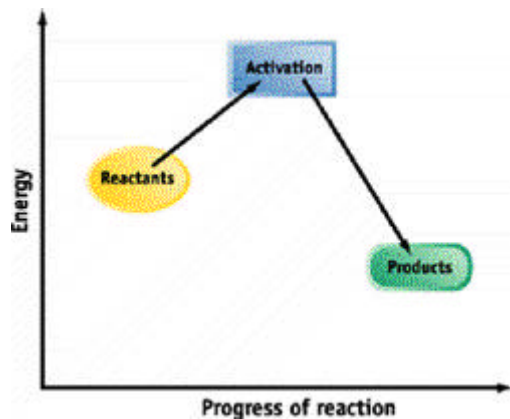
Catalytic processes take place when reactants are adsorbed onto the surface of a catalyst. The catalyst has "activation sites" that promote reaction. After reaction, the resulting products desorb from the catalyst surface and are carried away into the airstream, leaving open, fresh catalyst surfaces.

The catalytic process involves several key steps: the mass transfer of the reactants from the bulk fluid stream to the catalyst surface, adsorption of the reactants to the catalyst surface, the reaction activated at the catalyst surface, desorption of the products from the catalyst surface and mass transfer of products to the bulk fluid.

The following are typical examples of simple reactions.



Reactions 1, 2, 3a and 3b are exothermic and thermodynamically favorable. That is, the products have less energy than the reactants (see Fig. 1). However, when CO and O₂ (Reaction 1) are mixed at room



temperature, they exist without combining for an infinite amount of time. This is true for Reaction 2, involving a hydrocarbon/air mixture.

The reactions can take place at an elevated temperature, particularly when heated in a flame 1,600°F to 2,000°F. Reaction 1 can be facilitated in the presence of a manganese oxide bearing catalyst at ambient conditions. Likewise, methanol can be reacted completely into CO₂ and H₂O (see Reaction 2) at temperatures as low as 350°F over a precious metal catalyst. The primary function of catalysis is to enhance chemical reactions (by providing suitable pathways for the reaction to occur) without the catalyst being consumed as a reagent.

A catalyst such as platinum can convert ethylene to CO₂ and H₂O as in step 3a, which is not desired by chemical manufacturers. A selective catalyst, such as silver, yields the desired ethylene oxide as shown in step 3b. Thus, selectivity of a reaction path is important. The selectivity of the catalysts is an equally important consideration in catalysis as is the temperature of reaction.

Materials used for catalysts

Certain metals and metal-oxides have a natural propensity for enhancing the catalytic reaction. Among the precious metals are platinum, palladium and rhodium. Sometimes, they're combined.

Choosing a metal depends upon the application. Remember that catalysts are selective. A reaction may proceed in the presence of one catalyst and not at all in the presence of another. Other factors are important, too, such as cost and availability.

Environmental laws on occupational and public safety have become increasingly stringent about the use of metal catalysts. The laws make it more difficult -and more expensive- to dispose of base metal catalysts after their useful lives are over.

Then there's the issue of recovering spent precious metals from catalysis. Precious metal catalysts are efficient, easy to handle and easy to dispose of despite tighter environmental and legal constraints. Moreover, most of their intrinsic value (the value of the metal itself) is recoverable.

Selection of a specific catalyst material-and configuration-for a specific process is determined by the material's propensity to drive the desired reaction.

To work at peak efficiency, it must withstand reactions without becoming deformed or clogged with particulates. That allows the reactants to adhere easily to the catalyst activation sites and for products to be removed continuously from the catalyst surface.

Catalyst configuration

Catalysts for various applications are fabricated in a number of configurations including beads, pellets and monolithic structures. Each configuration offers clear advantages and disadvantages depending upon its use.

+Monolithic catalyst A monolithic catalyst is produced in three stages, each representing three physical parts of a fabricated catalyst. The first part is the refractory substrate, generally made of cordierite. The inert material is manufactured as a honeycomb structure.

Next, the catalyst manufacturer "washcoats" this substrate with a high surface area support material, typically gamma-alumina. That enhances the surface area of the substrate, providing better metal dispersion and decreasing sintering. By taking the flat surfaces of the cordierite and adding the washcoat, the structure now contains bumps, ridges and valleys to increase its surface area by 5000X. Besides increasing surface area, the washcoat helps impart the characteristics required for the catalytic process itself.

The third phase involves putting the metal onto the washcoat. In essence, the metals, which are in solution, are impregnated onto the surface of the washcoat through proprietary technology. That technology gives catalysts unique operating efficiencies and life cycles.

+Beads and pellets. The other approach to catalysis involves catalytic beads or pellets without a substrate carrier. Those configurations are produced from refractory alumina-the same material used to "washcoat" the monolithic honeycomb catalysts.

After the beads or pellets are fabricated, they are impregnated with one or more metals used for enhancing the procedure. In essence, the difference between a monolithic structure (or honeycomb) and a bead or pellet is merely one less manufacturing step. There is no support because the bead or pellet itself is the washcoat. In application, the beads and pellets are generally loaded into a horizontal tray-to a depth between 4 in and 7 in-and the process fluid stream flows in a vertical direction.

Application	Carbon Monoxide	Organic Compounds	Organic Compounds	Halogenated Compounds
Catalyst type	Monolith	Monolith	Pellets or beads	Monolith
Destruction efficiency	Over 98%	Over 98%	Over 98%	Over 98%
Operating temperature	350°F to 600°F	350°F to 700°F	550°F to 650°F	700°F to 850°F
Residence time	0.025 sec	0.035 sec	0.10 sec	0.10 sec
Poison resistance	Low	Low	Medium	Low
Pressure drop	Low	Low	Medium	Low
Cost per 1000 scfm exhaust	\$4,500	\$5,400	\$3,360	\$16,200

Monolithic vs. pelletized

The beads or pellets offer the advantage of a tortuous path. On the other hand, without a substrate, the surface area per unit volume ratio of the catalyst system is lower; thus, more catalyst is needed, leading to a larger reactor with a larger volume. It takes about four times the number of pellets (volumetrically) to achieve the reaction efficiency of the monolithic catalyst.

The difficult path provided by beads or pellets also protects against catalyst poisoning. If poisoning agents enter the process stream, the superficial layers of the catalysts are poisoned to a great extent. But, the subsequent layers are protected more than they would be in the monolith configuration.

The advantage of the monolithic surface channels is that they function as a bundle of parallel, single-pass reactors. Those configurations exhibit low pressure drops, more uniform distribution of the reactants and good heat transfer. With respect to heat transfer, the catalysts attain operating temperatures quickly, maintain more uniform temperatures and dissipate hot spots. The monolithic structure, because it's basically a cluster of tubes, allows the poisons in the discharge stream to pass through the catalyst, poisoning the product faster than would happen with the pellets.

Overall, monolithic catalysts are preferred in fast kinetic processes. Beads or pellets are preferred in a relatively slow kinetic process, although they are useable in some fast kinetic applications. Table 1 is a comparison of the reaction characteristics and types of reactions conducted with monolithic and pelletized catalysts.

+For more information on catalyst and catalyst selection - MetPro Corp., Systems Div., Harleysville, PA.

Application determines the catalyst

Selection of a catalyst depends upon the process. Platinum and palladium metals have a strong affinity for carbon monoxide destruction. They can operate at temperatures as low as 350°F or as high as 1,400°F. Most metal and oxide catalysts can't handle that wide temperature variation. In a system with simultaneous control of hydrocarbons and carbon monoxide, combinations of platinum, palladium, rhodium and iridium catalysts offer superior performance and can handle dynamic temperature and concentration ranges that other metal catalysts can't.

For hydrocarbons containing a long chain, aromatics and alcohols, platinum group metals in various ratios have proven most effective. They generally convert the organics completely. Platinum-palladium catalysts are used for light hydrocarbons such as methane, ethane and propane. Those materials provide higher efficiency than platinum alone. In general, platinum is the material of choice for intense reactions involving carbon monoxide and other hydrocarbon contaminants. The catalysts are powerful in the reaction of aromatic compounds that can't be handled by nonprecious metals at lower temperatures.

For other classes of compounds considered "priority pollutants," such as halogenated organics, the catalytic reactor must be fabricated from special materials like Hastelloy. Hastelloy resists corrosion and can withstand high temperatures.

The catalyst must react with the halogen compounds without rapid deactivation. For that application, chromium has performed well. Platinum catalysts have been shown to sustain high temperatures, resist rapid deactivation and maintain longer life cycles. In fact, platinum catalysts have become the industry standard.