Mitigate Air Pollution with Catalytic Technology

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Catalytic oxidation and catalytic reduction control emissions by chemically transforming pollutants. Learn what equipment is available and how it works to treat exhaust streams from stationary sources.

Regulations place limits on chemical process industries (CPI) facilities that emit pollutants such as volatile organic compounds (VOCs), carbon monoxide (CO), and nitrogen oxides (NOx). Catalytic oxidation, selective catalytic reduction (SCR), and nonselective catalytic reduction (NSCR) are becoming more widely used on exhaust streams from equipment such as boilers, ovens, and engines to effectively and efficiently control airborne pollutants.

This article describes these technologies and the mechanisms behind their operation.

An overview of oxidation and reduction

Catalysts reduce pollution by facilitating the conversion of a harmful pollutant to a less-harmful material that will undergo further processing or a benign product that will be released into the atmosphere. The transformation can occur by either an oxidation reaction or a reduction reaction; oxidation occurs when a reactant loses electrons, reduction when a pollutant gains electrons.

For example, oxygen can be added to a stream containing CO to convert the CO to carbon dioxide (CO_2) and heat via an oxidation reaction. The reductant, CO, is oxidized when it loses an electron to the oxidizer, oxygen, producing the product CO_2 and releasing heat:

$$2CO + O_2 \rightarrow 2CO_2 + \text{Heat}$$

Combustion is a common oxidation reaction, whereby VOCs (or other hydrocarbons) lose an electron to oxygen to produce CO_2, water, and heat:

$$C_xH_y + zO_2 \rightarrow xCO_2 + y/2\ H_2O + \text{Heat}$$
$$\text{where } z = x + y/4$$

To enable a reduction reaction, a reducing agent is added to the process stream to donate an electron. For example, in ammonia SCR, ammonia (NH_3) serves as the reductant. Oxygen reacts with NOx and NH_3 to produce nitrogen and water; NOx gains electrons and hydrogen when the NH_3 bonds with oxygen to form water; and nitrogen (from the NH_3 and the NOx) bonds with itself:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$$
$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$$

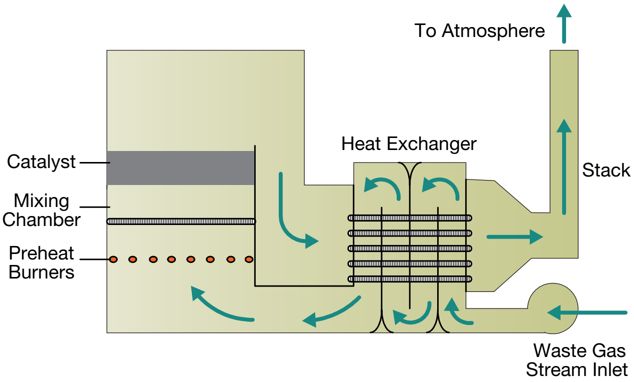
Nonselective catalytic reduction is another method for reducing NOx, in which CO present in the exhaust stream serves as the reductant:

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

Catalyst basics

Central to catalytic oxidation and catalytic reduction is the catalyst itself, which can be either homogeneous or heterogeneous. Homogeneous catalysts exist in the same phase as the reactants, typically solids or gases. Conversely, heterogeneous catalysts exist in a different phase than the reactants, most often as a solid with liquid or gaseous reactants.

For the control of the airborne pollutants discussed in



▲ **Figure 1.** To ensure complete oxidation in a catalytic oxidizer, the waste gas stream is preheated in a heat exchanger and mixed thoroughly with oxygen before it enters the oxidation catalyst bed.

this article, solid-state heterogeneous catalysts are used. These solid heterogeneous catalysts have "sticky" surfaces that readily adsorb the reactants. (This leads to an easy way to remember the difference between adsorption and absorption. In adsorption, molecules are "stuck" to the surface of the material, whereas during absorption, molecules of one substance are "sucked" into the structure of the other material.)

When reactants adsorb onto the surface of a catalyst, their electrons rearrange, which weakens the existing bonds and primes the reactants for the reaction. The close proximity of the reactants on the catalyst surface helps the reactants to form more easily into the desired products. Once the reaction occurs, the product(s) desorb (*i.e.*, the molecules detach) from the surface of the catalyst.

One key to choosing an effective catalyst is to choose one that readily adsorbs the reactants, but also allows the products to easily desorb from its surface.

A catalyst's affinity for the reactants and lack of affinity for the products is referred to as its selectivity. The appropriate catalyst for a specific reaction should be highly selective, as well as have a high reactivity. Reactivity is a measure of how sticky the surface of the catalyst is, and a high reactivity translates into a high rate of adsorption.

Catalytic oxidation

Oxidation catalysts, or two-way catalysts, are used to control emissions of two types of pollutants — CO and hydrocarbons (such as VOCs and nonvolatile hydrocarbons). The exhaust is first collected at the source and directed to the catalytic oxidizer inlet; depending on the temperature of the exhaust gas, it may be sent through a heat exchanger to be preheated. To ensure that the gas completely oxidizes, it is typically combined with oxygen in a mixing chamber. The gas then flows through the catalyst bed; catalysts are typically platinum-group metals, such as ruthenium, rhodium, palladium, osmium, iridium, and platinum. If the clean gas requires cooling, it is sent back through the heat exchanger. The clean, cool gas is then released into the atmosphere. Figure 1 illustrates this process.

The use of catalysts in the oxidation process allows the reaction to be carried out at a much lower temperature than in some other types of pollution control equipment. For example, thermal oxidizers require temperatures ranging from 500°F to 1,000°F, while a catalytic oxidizer can effectively operate between 600°F and 800°F. As a result, catalytic oxidation consumes less fuel and involves safer operating conditions.

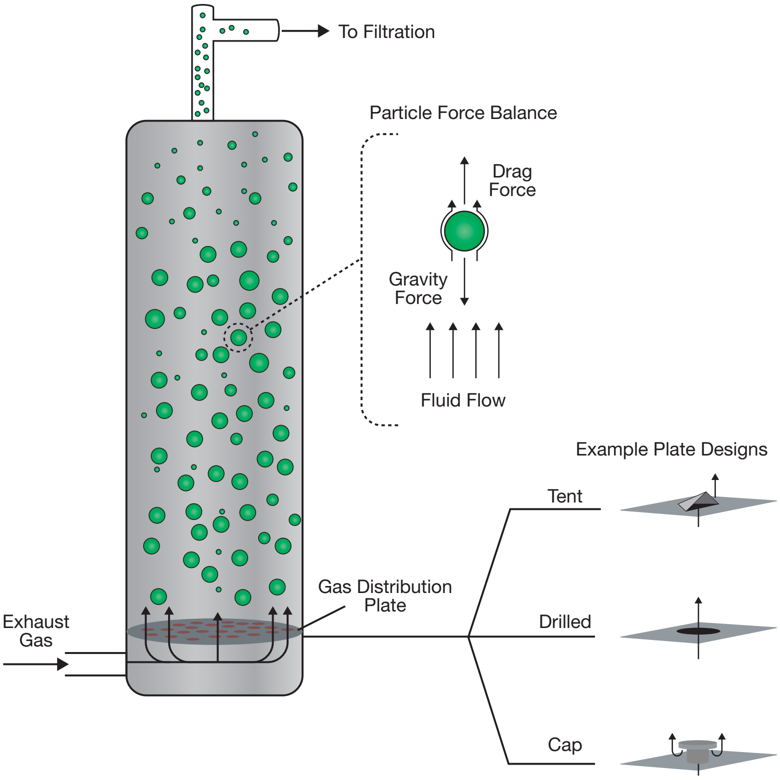
The catalyst beds in a catalytic oxidizer are either in a fixed-bed or fluid-bed arrangement. Fixed-bed systems are further classified as monolithic or packed-bed catalytic oxidizers.

In a monolithic setup (Figure 2), a solid, porous catalyst block with channels parallel to the direction of the flow rests on a ceramic or metallic base structure. During startup and shutdown, thermal expansion and contraction have little effect on operational effectiveness, and a consistent pressure is maintained over the catalyst. Monolithic catalytic oxidization is a commonly used technology for controlling air emissions from stationary combustion sources.

The packed-bed catalytic oxidizer employs a pelletized catalyst in a tube (or column) or shallow tray, which the exhaust gas passes through. Unlike the monolithic bed, the packed catalyst bed experiences a high pressure drop, which can cause the catalyst pellets to expand and degrade. In this arrangement, a portion of the pellets may be replaced periodically to maintain the catalyst activity. A packed-bed catalytic oxidizer is appropriate for applications where contaminants are present, as in the printing and

▲ **Figure 2.** This monolithic catalyst (shown here within a support structure) contains channels that allow gas to flow through the solid catalyst bed. Photo courtesy of MIRATECH.

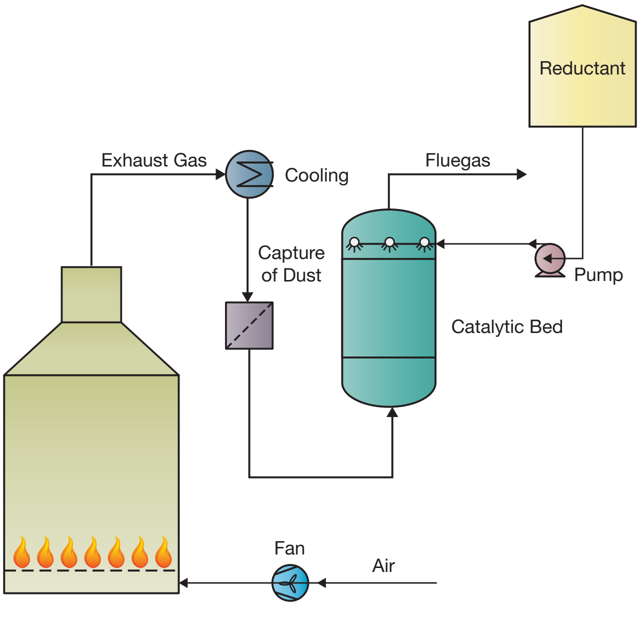
semiconductor manufacturing industries.



▲ **Figure 3.** In a fluidized-bed catalytic oxidizer, bubbles that form at the distribution plate rise and combine with other bubbles. As they rise, the bubbles burst and drive solid particles upward. In the areas where there are no bubbles and near the walls of the column, the particles are moving downward. This constant circulation of particles promotes axial mixing throughout the bed.

Fluid-bed catalytic oxidizers (Figure 3) also utilize catalysts in the form of pellets. However, the solid pellets are fluidized — *i.e.*, they are placed under operating conditions that enable them to behave as a fluid. The friction between the pellets removes particulate matter, which can extend the life of the catalyst by eliminating these potential fouling agents, although the friction can also contribute to attrition of the catalyst and lead to a decline in performance. Fluid-bed catalytic oxidizers have pressure drops slightly higher than those of fixed-bed monolithic catalytic oxidizers.

Catalytic oxidizers offer advantages over thermal oxidation (*i.e.*, incineration) that include lower operating temperatures, lower fuel consumption, the need for less insulation, a smaller equipment footprint, and a lower risk of fire or flashback because there is no flame *(1)*. Some disadvantages of catalytic oxidation include higher startup costs; catalyst susceptibility to poisoning from some process contaminants; the need, in some cases, for additional processing to remove particulates prior to oxidation to prevent catalyst plugging; and the need to dispose of the spent catalyst properly *(1)*. In addition, depending on the catalyst material, the service, and the pollutants that have been destroyed by the catalytic process, catalyst that cannot be recycled may be considered hazardous waste.



▲ **Figure 4.** Unlike other forms of catalytic pollution abatement, SCR requires the addition of a reductant, separate from the process stream, that must be pumped into the catalyst bed.

Selective catalytic reduction

SCR removes NOx from stationary pollution sources. The exhaust gas is injected, along with a reducing agent, into a reactor that contains a catalyst. When the reaction is complete, the product gas can be released into the atmosphere or further processed to remove other pollutants. Figure 4 illustrates this process.

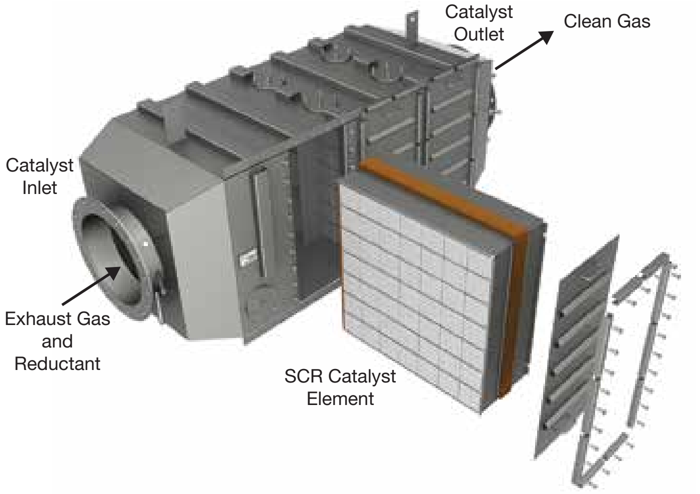
The most widely used SCR catalysts are metal oxides and zeolites. Metal-oxide-based catalysts, made of such materials as vanadium and titanium, are low cost and work well at temperatures ranging from 480°F to 800°F. Zeolite catalysts work at higher temperatures than metal-oxide catalysts, ranging from approximately 800°F to 1,000°F. They are also less likely to oxidize any sulfur dioxide (SO_2) that may be in the gas stream; SO_2 can combine with water to form corrosive sulfuric acid (H_2SO_4) or with unreacted ammonia to form ammonium sulfates that foul catalysts.

Catalysts have either a honeycomb or a plate configuration. The honeycomb arrangement has a high pressure drop and can easily become plugged by particulates in the gas stream. The larger plate design, though more expensive, has a lower pressure drop and is less susceptible to plugging. The SCR system in Figure 5 utilizes a honeycomb configuration.

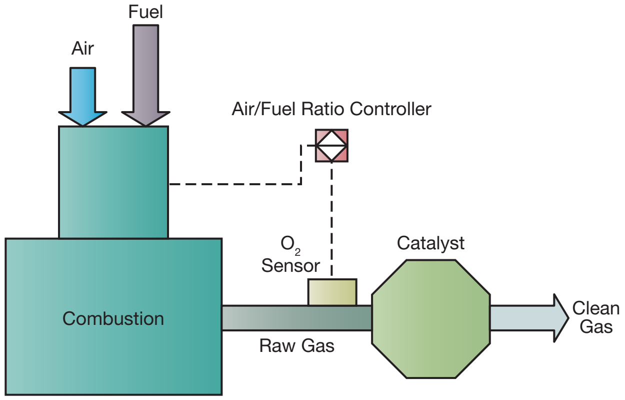
The addition of a reducing agent (reductant) distinguishes SCR from the other catalytic pollution-control technologies. Commonly used reductants include anhydrous ammonia, aqueous ammonia, and urea. Anhydrous ammonia requires no processing before injection, and smaller volumes are required so less material needs to be transported. However, it is extremely toxic and hard to store safely. Aqueous ammonia is safer to store, but it must be hydrolyzed before use. Urea is the safest reductant from a storage and handling perspective, but in most cases it must be converted to ammonia through thermal decomposition prior to injection.

Selective catalytic reduction systems achieve lower NOx levels than noncatalytic methods such as dry low-NOx (DLN) burners and selective non-catalytic reduction: SCR can achieve NOx levels as low as 2 ppm, whereas DLN burners can only achieve 5–15 ppm, and SNCR approximately 80 ppm. SCR is also effective on streams with NOx concentrations as low as 20 ppm, while SNCR requires a stream with at least 200 ppm to 400 ppm NOx *(2)*. And, SNCR systems require temperatures of 1,600°F to 2,100°F, but SCR operates in the relatively low range of 480°F to 1,000°F *(2)*.

SCR's effective reduction of NOx comes with high installation and maintenance costs. The systems are costly to install or retrofit, and require large amounts of catalyst and reagent during operation. A major maintenance requirement is periodic cleaning of downstream equipment to remove aerosols generated in the SCR system and any ammonia in the exiting waste gas (*i.e.*, ammonia slip) *(2)*.



▲ **Figure 5.** This SCR catalyst housing is configured to accomodate up to three catalyst elements (only one is shown here). Photo courtesy of MIRATECH.



▲ **Figure 6.** The NSCR system requires a balance of air to fuel that is monitored by an oxygen sensor. Achieving the appropriate air-to-fuel ratio is key to effectively eliminating pollutants from the gas stream.

Nonselective catalytic reduction

NSCR (Figure 6) combines catalytic oxidation and catalytic reduction into a single system that mitigates NOx, CO, and VOCs. Because these systems destroy three different categories of pollutants, the catalysts are often referred to as three-way catalysts. NSCR works like catalytic oxidation, with the addition of a reduction reaction that uses the CO present in the exhaust stream as the reductant to convert NOx to nitrogen.

The catalytic converter in automobiles, which has played a major role in reducing automobile-related air pollution, is an NSCR system. Additionally, NSCR is often utilized for stationary sources that operate at a rich fuel-to-air ratio, such as four-stroke rich-burn reciprocating internal-combustion engines. The term rich refers to a stoichiometric excess of fuel; the inverse is lean, where there is an excess of air. Rich-burn engines benefit from NSCR's ability to destroy NOx, CO, and VOCs simultaneously. Because emissions from lean-burn engines already have low NOx emissions, they require only an oxidation catalyst for the destruction of CO and VOCs.

Rich-burn engines employing NSCR must have a tightly controlled air-to-fuel ratio to ensure that the CO and VOCs are oxidized and the NOx is reduced. If the mixture becomes too rich, there will not be enough oxygen available for the reactions. As a result, NSCR systems include an oxygen sensor to provide feedback to the air-to-fuel ratio controller.

Selection and maintenance

Factors to consider in the selection and installation of a catalytic air-pollution-control system include operating temperature, residence time, catalyst surface area, air-to-

Table 1. Comparison of the three types of catalytic technology appropriate for air pollution control.

	Catalytic Oxidation	Selective Catalytic Reduction (SCR)	Nonselective Catalytic Reduction (NSCR)
Pollutants Controlled	CO VOCs	NOx	NOx CO VOCs
Additional Reactants	O_2 (from the atmosphere)	Anhydrous ammonia Aqueous ammonia Urea	O_2 (from the atmosphere) CO (from the exhaust stream)
Common Catalyst(s)	Platinum Palladium	Vanadium Titanium oxides Zeolite	Platinum Palladium Rhodium
Operating Temperature	600°F–800°F	Vanadium: 480°F–800°F Zeolite: 800°F–1,000°F	800°F–1,200°F
Concentration Achievable	CO: 2 ppmvd VOCs: 1 ppmvd	NOx: 2 ppmvd	NOx: 10 ppmvd CO: 2 ppmvd VOCs: 1 ppmvd
Other Technologies to Consider	Thermal Incineration	Dry Low-NOx (DLN) Burner Selective Non-Catalytic Reduction (SNCR) Steam/Water Injection	SCR + Thermal Incineration Catalytic Oxidation + SCR

Note: The data in this table are approximate and intended only as a general estimate. Actual data will vary based on the application, requirements, and site-specific information. All concentrations are corrected to 15% O_2. Source: Adapted from Refs. 3–6.

waste-gas ratio, type and concentration of pollutants, and the presence of any contaminants that could contribute to masking or fouling. Table 1 summarizes some of the requirements and attributes for the three types of catalytic systems discussed.

Although the catalysts are not appreciably consumed during operations, they do require maintenance and monitoring. They may become altered by masking or fouling agents or through unintended chemical or physical change.

Catalyst effectiveness can be estimated by monitoring the pressure drop across the bed and the exhaust gas inlet and outlet temperatures, as well as periodic testing and use of a continuous emissions monitoring system (CEMS). If any of these parameters indicate that the catalyst is not functioning properly, depending on the type of catalyst, corrective actions may include replacement, washing, or regeneration of the catalyst.

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