A catalytic converter is a device used to reduce the emissions from an internal combustion engine (used in most modern day automobiles and vehicles). Not enough oxygen is available to oxidize the carbon fuel in these engines completely into carbon dioxide and water; thus toxic by-products are produced. Catalytic converters are used in exhaust systems to provide a site for the oxidation and reduction of toxic by-products (like nitrogen oxides, carbon monoxide, and hydrocarbons) of fuel into less hazardous substances such as carbon dioxide, water vapor, and nitrogen gas.

Introduction

Catalytic converters were first widely introduced in American production cars in 1975 due to EPA regulations on toxic emissions reductions. The United States Clean Air Act required a 75% decrease in emissions in all new model vehicles after 1975, a decrease to be carried out with the use of catalytic converters. Without catalytic converters, vehicles release hydrocarbons, carbon monoxide, and nitrogen oxide. These gases are the largest source of ground level ozone, which causes smog and is harmful to plant life. Catalytic converters can also be found in generators, buses, trucks, and trains—almost everything with an internal combustion engine has a form of catalytic converter attached to its exhaust system.

A catalytic converter is a simple device that uses basic redox reactions to reduce the pollutants a car makes. It converts around 98% of the harmful fumes produced by a car engine into less harmful gases. It is composed of a metal housing with a ceramic honeycomb-like interior with insulating layers. This honeycomb interior has thin wall channels that are coated with a washcoat of aluminum oxide. This coating is porous and increases the surface area, allowing more reactions to take place and containing precious metals such as platinum, rhodium, and palladium. No more than 4-9 grams of these precious metals are used in a single converter.

The converter uses simple oxidation and reduction reactions to convert the unwanted fumes. Recall that oxidation is the loss of electrons and that reduction is the gaining of electrons. The precious metals mentioned earlier promote the transfer of electrons and, in turn, the conversion of toxic fumes.
The last section of the converter controls the fuel-injection system. This control system is aided by an oxygen sensor that monitors how much oxygen is in the exhaust stream, and in turn tells the engine computer to adjust the air-to-fuel ratio, keeping the catalytic converter running at the stoichiometric point and near 100% efficiency.

**Functions**

A three-way catalytic converter has three simultaneous functions:

1. Reduction of nitrogen oxides into elemental nitrogen and oxygen: \[\text{NO}_x \rightarrow \text{N}_x + \text{O}_x\]
2. Oxidation of carbon monoxide to carbon dioxide: \[\text{CO} + \text{O}_2 \rightarrow \text{CO}_2\]
3. Oxidation of hydrocarbons into carbon dioxide and water: \[\text{C}_x\text{H}_{4x} + 2x\text{O}_2 \rightarrow x\text{CO}_2 + 2x\text{H}_2\text{O}\]

There are two types of "systems" running in a catalytic converter, "lean" and "rich." When the system is running "lean," there is more oxygen than required, and the reactions therefore favor the oxidation of carbon monoxide and hydrocarbons (at the expense of the reduction of nitrogen oxides). On the contrary, when the system is running "rich," there is more fuel than needed, and the reactions favor the reduction of nitrogen oxides into elemental nitrogen and oxygen (at the expense of the two oxidation reactions). With a constant imbalance of the reactions, the system never achieves 100% efficiency.

Note: converters can store "extra" oxygen in the exhaust stream for later use. This storage usually occurs when the system is running lean; the gas is released when there is not enough oxygen in the exhaust stream. The released oxygen compensates for the lack of oxygen derived from NO\(_x\) reduction, or when there is hard acceleration and the air-to-fuel ratio system becomes rich faster than the catalytic converter can adapt to it. In addition, the release of the stored oxygen stimulates the oxidation processes of CO and \(\text{C}_x\text{H}_{4x}\).

**Dangers of pollutants**

Without the redox process to filter and convert the nitrogen oxides, carbon monoxides, and hydrocarbons, the air quality (especially in large cities) becomes harmful to the human being.

**Nitrogen oxides:** These compounds are of the same family as nitrogen dioxide, nitric acid, nitrous oxide, nitrates, and nitric oxide. When NO\(_x\) is released into the air, it reacts, stimulated by sunlight, with organic compounds in the air; the result is smog. Smog is a pollutant and has adverse effects on children’s lungs. NO\(_x\) reacting with sulfur dioxide produces acid rain, which is highly destructive to everything it lands on. Acid rain corrodes cars, plants, buildings, national monuments and pollutes lakes and streams to an acidity unsuitable for fish. NO\(_x\) can also bind with ozone to create biological mutations (such as smog), and reduce the transmission of light.
Carbon monoxide: This is a harmful variant of a naturally occurring gas, CO$_2$. Odorless and colorless, this gas does not have many useful functions in everyday processes.

Hydrocarbons: Inhaling hydrocarbons from gasoline, household cleaners, propellants, kerosene and other fuels can be fatal to children. Further complications include central nervous system impairments and cardiovascular problems.

Catalytic inhibition and destruction

The catalytic converter is a sensitive device with precious metals coating the inside. Without these metals, the redox reactions cannot occur. There are several substances and chemicals that inhibit the catalytic converter.

1. Lead: Most vehicles run on unleaded gasoline, in which all the lead has been removed from the fuel. However, if lead is added to the fuel and is burned, it leaves a residue that coats the catalytic metals (Pt, Rh, Pd, and Au) and prevents contact with the exhaust fumes, which is necessary in performing the necessary redox reactions.

2. Manganese and silicon: Manganese is primarily found in the organometallic compound MMT (methylcyclopentadienyl manganese tricarbonyl). MMT is a compound used in in the 1990's to increase fuel's octane rating (a higher octane rating indicates that the gas is less likely to combust, causing the engine to explode. This is important since higher performing engines have a high compression ratio, which would need a higher octane gas to complement the amount of compression in the engine), and has now been banned from commercial sale due to the EPA's regulations. Silicon can leak from the combustion chamber into the exhaust stream from the coolant inside the engine.

These contaminants prevent the catalytic converter from functioning properly. However, this process could be reversed by running the engine at a high temperature to increase the hot exhaust flow through the converter, melting or liquefying some of the contaminants and removing them from the exhaust pipe. This process does not work if the metal is coated with lead, because lead has a high boiling point. If the lead poisoning is severe enough, the whole converter is rendered useless and must be replaced.

Thermodynamics of catalytic converters

Recall that thermodynamics predicts whether or not a reaction or process is spontaneous under certain conditions,
but not the rate of the process. The redox reactions below occur slowly without a catalyst; even if the processes are thermodynamically favorable, they cannot occur without proper energy. This energy is the activation energy ($E_a$ in the figure below) required to overcome the initial energy barrier preventing the reaction. A catalyst aids in the thermodynamic process by lowering the activation energy; the catalyst itself does not produce a product, but it does affect the amount and the speed at which the products are formed.

1. Reduction of nitrogen oxides into elemental nitrogen and oxygen: \[NO_x \rightarrow N_x + O_x \]
2. Oxidation of carbon monoxide to carbon dioxide. \[CO + O_2 \rightarrow CO_2 \]
3. Oxidation of hydrocarbons into carbon dioxide and water. \[C_xH_{4x} + 2xO_2 \rightarrow xCO_2 + 2xH_2O \]

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Catalytic converter theft

Due to the precious metals in the coating of the inner ceramic structure, many catalytic converters have been targeted for theft. The converter is the most easily-accessible component because it lies on the outside and under the car. A thief could easily slide under the car, saw the connecting tubes on each end, and leave with the catalytic converter. Depending on the type and amount of precious metals inside, a catalytic converter can be easily sold for $200 apiece.
Global Warming

Although the catalytic converter has helped reduce toxic emissions from car engines, it also has detrimental environmental effects. In the conversion of hydrocarbons and carbon monoxide, carbon dioxide is produced. Carbon dioxide is one of the most common greenhouse gases and contributes significantly to global warming. Along with carbon dioxide, the converters sometimes rearrange the nitrogen-oxygen compounds to form nitrous oxide. This is the same compound used in laughing gas and as a speed enhancer in cars. As a greenhouse gas, nitrous oxide is a 300 times more potent than carbon dioxide, and contributes proportionally to global warming.

References


Problems

1. What are the potential hazards of the toxic substances emitted by a car without a catalytic converter?
2. Which 3 redox reactions occur in a three-way catalytic converter?
3. Does the catalytic converter run at 100% efficiency? Why or why not?
4. How can catalytic converters be damaged or misused?
5. Why are catalytic converters targeted for theft?

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