Module 5:Emission Control for SI Engines

Lecture 24:Lean de-NOx Catalysts and Catalyst Poisoning

The Lecture Contains:

- Lean de-NO_X Catalysts
- NO_X storage-reduction (NSR) catalyst
- SCR Catalysts
- CATALYST DEACTIVATION
- Catalyst Poisoning

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Lean de-NO_x Catalysts

The gasoline direct injection (GDI) engine operating in stratified charge mode is a a lean-burn spark-ignited engine that gives 20 – 30% higher fuel efficiency compared to the conventional stoichiometric engine The diesel engines also operate with 40% or more excess air. The 3-way catalytic converter cannot provide NO_x reduction in the lean burn SI and the diesel engines. Lean de-NO_x catalyst technology has been developed to meet the needs of these engines. Two main types of lean de-NO_x catalyst technology are;

- NOx storage-reduction (NSR) catalyst or NO_x trap
- Selective catalytic reduction (SCR)

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NOx storage-reduction (NSR) catalyst

In the NSR catalysts NO_x is trapped under oxygen-rich conditions in an alkaline earth material like BaO which is incorporated in the noble-metal containing washcoat of 3-way catalyst. The NO_x trap concept is shown schematically in Fig. 5.24 .

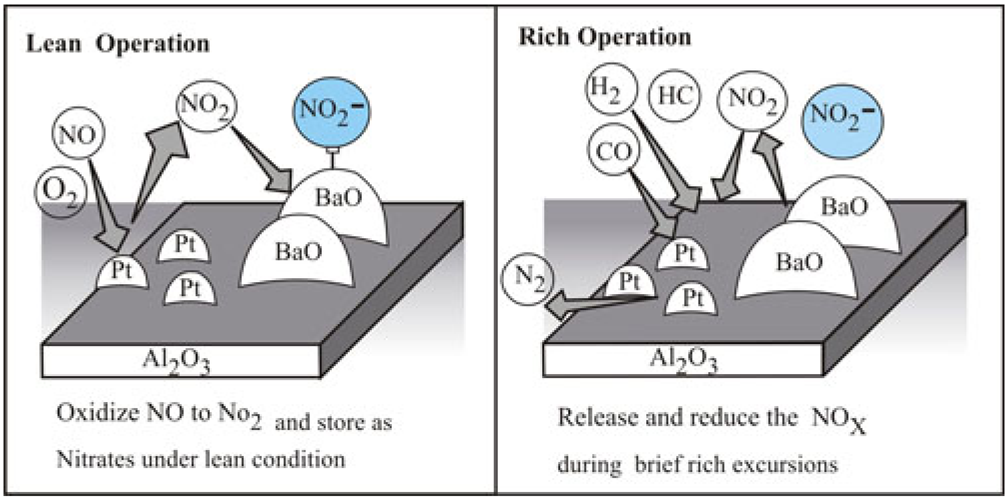

Figure 5.24	Schematic of a NSR Catalyst (NO x trap).

NO is first converted to NO_2 over Pt catalyst from the oxygen rich exhaust

$$NO + O_2 \xrightarrow{PT} NO_2 \quad (5.7)$$

The NO_2 is temporarily stored on alkaline metal oxide BaO forming its nitrate,

$$NO_2 + BaO \rightarrow BaO \bullet NO_2 \quad (5.8)$$

The trap is saturated with NO_x in about 60 seconds. A precisely controlled spike of rich mixture is then supplied to the engine so that HC and CO in significant amounts are present in the gases. The required rich mixture for SI engine may be obtained by the

synchronized control of fuel injection pulse width. The stored NOx is reduced by the HC and CO) during a short period of about a second.. The NO_x reduction takes place on a noble metal catalyst.

$$BaO \bullet NO_2 + HC \rightarrow BaO + N_2 + H_2O + CO_2 \quad (5.9)$$

Lean NO_x traps have high conversion efficiency in a relatively narrow temperature range of 350 –450º C. However, different vehicle operating modes produce widely differing exhaust gas temperatures and the overall conversion efficiency of NSR catalysts is 30 to 35% only. Another problem is poisoning of the trap by fuel sulphur. Fuel sulphur of less than 5 ppm is necessary for operation of NSR catalysts.

SCR Catalysts

Selective reduction catalysts applied in SI engines work on the principle of direct reduction of NO_X by hydrocarbons injected into exhaust stream. In the diesel engines the SCR system uses ammonia produced from urea is used as the reducing agent or ‘reductant'. The urea SCR systems would be discussed in detail in Module 6. In the lean-mixture environment, NO_X may be reduced by HC as per the following reaction:

$$HC + NO_x + O_2 \rightarrow N_2 + CO_2 + H_2O \qquad (5.10)$$

The exhaust gas stream should have right type of HC in right concentrations to complete the above reaction and reduce nitrogen oxides. Propane is effective at around 500º C and ethylene at 160-200º C. Zeolites like Cu/ZSM-5 have been studied as SCR catalysts. However, these catalysts are sensitive to water vapour and sulphur dioxide, and hence so far, have had only a limited success.

CATALYST DEACTIVATION

The automotive catalysts in the USA are required to meet the emission standards for 192,000/240,000 km. of life, The fresh catalysts while meet the standards but during vehicle operation their conversion efficiency deteriorates due to ageing and poisoning effects by the contaminants that may come from fuel or engine lubricating oil that burns in the cylinder. The catalyst is subjected to high temperatures exceeding 900 ºC, thermal shocks and mechanical vibrations. Contaminants originating from fuel that cause serious catalyst poisoning, are sulphur and lead (now the gasoline is free of lead), and from lubricating oil are zinc and phosphorous compounds.

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The catalyst deactivation causes ;

- Increase in light off temperature, and
- Decrease in maximum conversion efficiency

Two types of catalyst of deactivation are encountered in practice:

- Catalyst poisoning
- Thermal deactivation

Catalyst Poisoning

The contaminants can poison the catalyst in the following manner:

- Deposition on the active catalyst sites chemically reacting with catalyst
- Accumulation of the contaminants on the outer surface of the catalyst physically restricting contact of the exhaust gases with the catalyst. This is termed as ‘blanketing effect'.

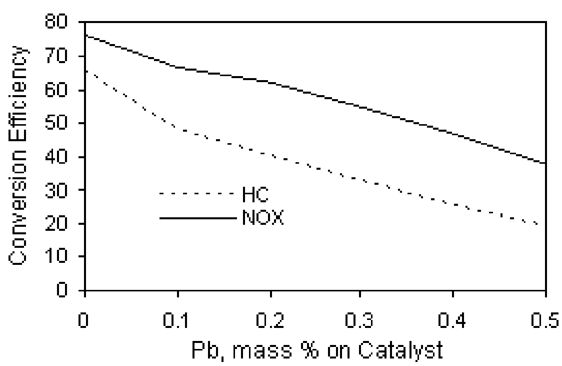

Figure 5.25	Effect of lead poisoning on a 3-way catalytic converter.

Lead as tetra ethyl lead was used for many years as antiknock additive in gasoline. Lead oxides and other lead compounds formed during combustion cause very rapid degradation of the catalyst performance. About 10 to 30 percent of the lead in the fuel gets deposited on the catalyst sites and catalyst washcoat. A typical effect of lead on the conversion efficiency of a Platinum/Rhodium 3- way catalyst is shown on Fig. 5.25. A lead deposition of about 0.5 % of catalyst weight causes 50% drop in the conversion efficiency. Now, the gasoline almost all over the world is lead free.

Sulphur naturally occurs and is present in small amounts in petroleum fuels It causes catalyst poisoning, Pd being more sensitive than Pt and Rh.. In a test, after 160,000 km vehicle operation fuel with sulphur of 575 ppm increased the catalyst light off temperature to 299º C from 277 º C with 40 ppm sulphur fuel.

Zinc and phosphorous additives used in lubricating oil get converted to oxides during combustion and form zinc pyrophosphate glaze over large areas of the catalyst surface, which seals the passage of exhaust gas to the catalyst sites. Silicon coming from contamination of fuel clogs the protective sheath of the sensor restricting the diffusion of gases to the surface of the sensor element. It affects the response of oxygen sensor which adversely affects conversion efficiency of the closed loop controlled three-way catalysts.