The Lecture Contains:

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Thermal Deactivation

During normal city driving, exhaust temperatures are normally below 600° C. However, overheating of catalyst may occur due to engine malfunction such as ignition failure, misfire or excessively rich operation. The very high concentration of unburned hydrocarbons in exhaust when oxidized in converter leads to excessively high catalyst bed temperatures. When the catalyst is exposed to temperatures above 900-1000 °C, loss in catalyst surface area and loss in dispersion of catalyst particles due to sintering are obtained. Ignition failure for about 20 seconds may completely destroy the catalyst.

Sintering caused by high temperatures results in;

- Under high temperatures, the catalyst particles migrate, coalesce or atoms in vapour phase get transported from smaller particles to larger particles. These process form large particles by combination of several small catalyst particles. Thermal sintering of the catalyst particles reduces catalyst activity.
- As the temperature increases to 1200° C, γ -alumina changes to α -alumina resulting in washcoat shrinkage, loss of micro-pores and reduction in catalyst surface area by a factor of 10. The catalyst particles are also trapped inside the collapsed pores which then are unable to come into contact with the gases.
- Thermal deactivation increases light off temperature. After ageing at 730° C, the catalyst had a surface area of 21.5 m^2/g of washcoat that reduced to 11.4m^2/g after ageing at 1000° C. The corresponding light off temperatures were about 250 and 320° C, respectively.

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Module 5:Emission Control for SI Engines

Lecture 25:Thermal Catalytic Deactivation, Summary of SI Emission Control

contd..

The sintering of precious metal and wash coat are shown schematically on Fig. 5.26 ..

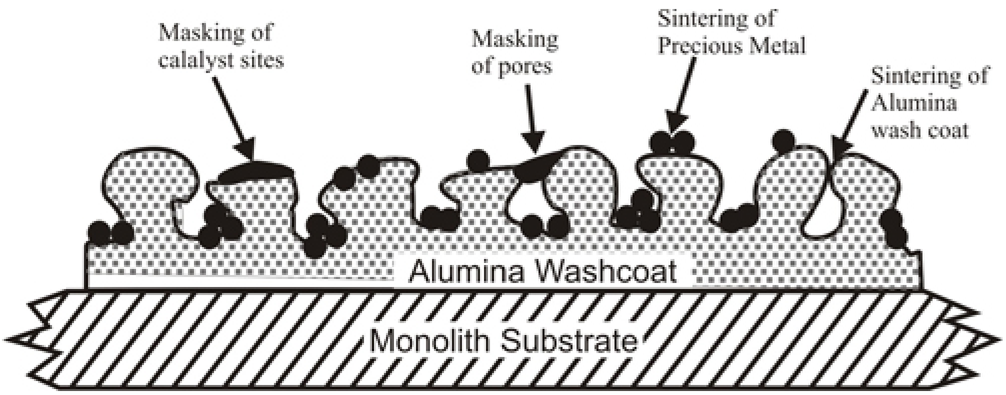

Figure 5.26	Conceptual representation of sintering of noble metal and washcoat material and masking of catalyst sites by contaminants

For the ceramic monolith catalytic converters, the temperature limit during 1990's was about 900° C. Improvements in the washcoat technology and use of metallic monoliths has raised this limit to around 1050°C . The correlation of different deactivation mechanisms of 3-way catalysts with operating temperature is summarized in Fig. 5.27 . The preferred operating range of the catalysts has gone up from 400 –700° C in 1980s to a maximum temperature of 1000° C in 1990s through development of better washcoat and catalyst formulations. The catalytic converters now are being mounted very close to the engine for cold engine emission control and hence higher catalyst temperatures Development of new substrate materials like SiC has contributed to catalyst operation at much higher temperatures than before.

	Temperature, ºC	Effect on Catalyst
	1700	High Temperature Ceramic melts
	1500	Standard Cordierite Monolith Melts
	1400	
		Cordierite phase changes to Mullite
	1300	Washcoat deterioration ?– Alumina changes to a - Alumina
	1100	
	900	Pt-Pd alloy forms in oxidizing A/F
		Diffusion of Rh_2O_3 in Al_2O_3 ,

		Alumina begins sintering
optimum Range	800	
		Pt-Pd and Pt-Rh alloy forms in Reducing A/F
	700	Platinum sinters
		Reaction of Zn and P with washcoat
	500	
	300	Catalyst Light-off
NO CONVERSION		
	100	

Figure 5.27	Summarized view of effect of operating temperature on functioning and deactivation of 3-way catalysts

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Summary of SI Engine Emission Control

The emission control technologies adopted since the emission standards were implemented for the first time in the USA are summarized in Table 5.4.

Table 5.4

Summary of Developments in Emission Control Technology for Gasoline Passenger Cars

Model Year	Technology
1963	Positive crankcase ventilation (PCV) system
1968	Evaporative emission control
1973	EGR, Secondary air injection, Thermal reactor, Spark advance ontrol
1975	Oxidation catalytic converter for CO and HC, Lead-free gasoline
1977	4-Valve combustion chambers
1981	3-Way catalysts for control of CO, HC and NO_x, λ-sensor, and electronic control
1988	Variable valve timing and lift, VVT, Honda VTEC
1990	Port fuel injection (PFI) universally adopted, death of carburetor
1994	Onboard Diagnostics (OBD) systems
1996	First DISC engines by Mitsubishi and Toyota, de-NO_x catalysts
1999	Phasing in of LEV standards, closed-coupled catalysts
2004	HC- adsorber/traps catalysts, thin wall substrates

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Questions

(5.1) What is the significance of space velocity of a catalytic converter? A gasoline car powered by a 1.2 litre swept volume engine is fitted with a catalytic converter of 1.2 litre. The maximum speed of the engine is 5,500 rpm and when operating at maximum load it has volumetric efficiency of 0.8. Taking inlet conditions as 100 kPa, 300K and stoichiometric mixture, calculate the maximum space velocity encountered in the converter if the exhaust gas enters the catalyst at 500 K. Take gasoline as octane.

(5.2) In the above converter, exhaust gas with 1.2% CO and 1000 ppmC1 HC enters. If conversion efficiency of the converter is 90 % for CO and HC, estimate increase in the gas temperature under steady state operation of the engine and converter. The LHV of gasoline is 44 MJ/kg and of CO is 10.1 MJ/kg. The specific heats of gases are: N_2 = 33.75, O_2 = 35.59, CO2 = 55.37, H_2O = 44.94 kJ/kmol.K

(5.3) In a gasoline car exhaust gas with 9.0, 0.8 and 0.6 g/km of CO, HC and NO_x enters the 3-way catalytic converter. During city trip of 15 km for the first 1.5 km the exhaust gas temperatures being low the catalyst has overall only 20% conversion efficiency. For the remaining trip, efficiency of conversion is 85%. Find the average vehicle emissions for the trip in g/km.

(5.4) An inventor claims that he has developed a non-catalyst thermal reactor when fitted in the exhaust muffler converts HC and CO by 50%. Under the full engine load peak combustion pressure are about 40 bar and temperature is 2500 K. Under the other conditions the peak combustion temperatures and pressures would be lower than these. The exhaust blows down to 1.1 bar pressure. The polytropic index of expansion process is about 1.28. As the gas flows through the exhaust pipe its temperature falls by 50% when it reaches the exhaust muffler. The residence time for the exhaust gas in the muffler is 100 ms. In view of the above information verify the acceptability of these claims.

(5.5) An engine misfires and HC concentration in the exhaust gas suddenly rises to 50,000 ppmC1. Estimate the extent of sudden increase in the gas and catalyst temperatures for a ceramic monolith converter. The converter volume is 0.85 litre, mass 340 g, specific heat is 0.9 kJ/kg. K.

(5.6) If the engine in Problem 5.5 is fitted with metal monolith converter of the same size having mass of 680 g and specific heat of 0.5 kJ/kg.K what would be the maximum temperatures reached. Assume the unburned HC are like gasoline in composition and have the same LHV as given in Problem 5.2.

(5.7) For cold start emission control discuss the advantages and disadvantages of the closed coupled catalysts, electric heated catalysts and HC traps.

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