Appendix 6
Background to the operation of three ways catalysts

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In the late 1970s it was discovered that certain precious metal combinations, most notably platinum (Pt) and rhodium (Rh), could simultaneously oxidise carbon monoxide and hydrocarbons (primarily via the Pt), and reduce oxides of nitrogen (primarily via the Rh) provided that the air to fuel ratio was maintained near stoichiometric. This was the birth of the three-way catalysts (TWC). The key to advancing the new TWC technology was to control the air to fuel ratio at all times within a narrow window of about ± 0.05 around the stoichiometric air to fuel ratio point of about 14.6:1 (on a weight basis). This became possible with the development of the oxygen, or lambda, sensor which is positioned immediately before the catalyst in the exhaust manifold. The voltage generated by the sensor is strongly dependent on the oxygen concentration. The sensor's voltage signal is fed back to the engine's ECU (a computer) which adjusts the air to fuel ratio, at a frequency of 0.5 to 1 times a second, by controlling the duration (thence quantity) of fuel supplied by the electronically actuated fuel injectors. This relatively simple closed loop feedback system controls the air to fuel ratio within the narrow window that allows the simultaneous conversion of all three pollutants. TWC technology was first installed in vehicles in 1979. Even today, this is the state of the art in air to fuel ratio control in petrol engines **and is critical for the efficient use of the TWC**.

TWC are primarily composed of about 0.1 to 0.15% precious metals with a Pt to Rh ratio of about 5:1 mixed with a ceramic support material (γ-alumina stabilised with other oxides and containing an oxygen storage material, usually cerium oxide). This composite washcoat is then deposited on a ceramic honeycomb typically having 400 cells per square inch. The oscillatory nature of the air to fuel ratio means that the catalyst will see slightly rich and slightly lean conditions alternatively, approximately 0.5 to 1 times a second. When operating lean the CO and HC are oxidised by the oxygen available in the exhaust, and the oxygen storage component is regenerated. When operating rich the oxygen storage component liberates adsorbed oxygen to consume the unreacted CO and HC. The ability of the catalyst to operate efficiently is, therefore, dependent on it maintaining a sufficient oxygen storage capacity (often known as the OSC) and the engine's control system providing both the correct range of lambda and at the right frequency.