(*ii*) The three main classes of gaseous pollutants are: CO and hydrocarbons (from incomplete combustion of the fuel) and oxides of nitrogen (NO_x, produced by fixing nitrogen in air).

Engine modification (such as exhaust gas recirculation, EGR) was sufficient to achieve the reduced emissions of CO and HC required in the USA in the 1970s. Tightening legislation since then has been met by the development of control strategies based on heterogeneous catalysis. To begin with, an oxidation catalyst (typically $Pt–Pd/Al_2O_3$) was fitted into the exhaust system, together with an additional supply of air. Oxidation of CO (to CO_2, reaction A2) and of HC (to CO_2 and H_2O) reduced the levels of these pollutants. At this stage, the NO_x limits could still be met by EGR.

$$2CO + O_2 = 2CO_2 \tag{A2}$$

The dual-bed catalyst was developed in response to the next phase of legislation, which imposed tighter limits on NO_x in particular. The system comprised two catalyst beds arranged sequentially in a single canister. The first bed catalysed the conversion of NO_x into N_2 under reducing conditions, by exploiting the presence of reductants, especially CO (reaction A3) in the exhaust stream.

$$2CO + 2NO = N_2 + 2CO_2 \tag{A3}$$
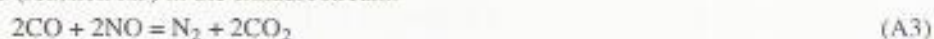
The second bed contained an oxidation catalyst; an additional supply of air was injected ahead of this bed to ensure optimum conversion of CO and HC.

This dual-bed system was made redundant by the development of the three-way catalyst – a single (but multi-component) catalyst capable of the simultaneous conversion of all three classes of pollutants.

(*iii*) The behaviour of many metallic oxides as catalysts for partial oxidation reactions can be rationalized in terms of a two-step redox mechanism (Mars and van Krevelen mechanism):

Step 1 $R + cat{-}O \longrightarrow RO + cat{-}$
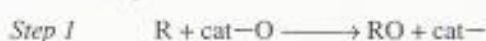
The hydrocarbon (R) is adsorbed and reacts with the catalyst surface at sites containing oxygen (cat$-$O). These sites are reduced.

Step 2 $\frac{1}{2}O_2 + cat{-} \longrightarrow cat{-}O$

The reduced sites (cat$-$) are replenished by oxygen from the gas phase; that is, they are oxidized.

It is the nature of the oxygen at the catalytic sites that is the key to the mechanism. Lattice oxygen (O^{2-}) can migrate to the surface and act as a more versatile oxidizing agent for hydrocarbons than molecular oxygen from the gas phase. (The lattice oxygen mechanism is not exclusive; for example, other species, such as O_2^- and O^-, may be involved.)

As the mechanism indicates, the catalyst must be capable not only of reduction, but also of subsequent reoxidation: for this reason it contains metals that can readily change their oxidation state to facilitate the redox process.
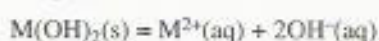
PART II

Question 7

(*a*) $E^{\ominus}$ for the following couple

$$M(OH)_2(s) + 2e = M(s) + 2OH^-(aq) \tag{13}$$

is just the value of E for the (M^{2+}|M) couple when the activity of *hydroxide* ions is unity (that is, $a(OH^-) = 1$), such that $a(M^{2+})$ is determined by the solubility product of $M(OH)_2$, as follows:

$$M(OH)_2(s) = M^{2+}(aq) + 2OH^-(aq)$$

so

$$K_{sp}^{\ominus} = \frac{a(M^{2+})\{a(OH^-)\}^2}{a(M(OH)_2)}$$

$$= a(M^{2+})\{a(OH^-)\}^2, \text{ since } a(M(OH)_2) = 1$$

$$= 5.48 \times 10^{-15}$$

So $a(M^{2+}) = 5.48 \times 10^{-15}$, with $a(OH^-) = 1$