



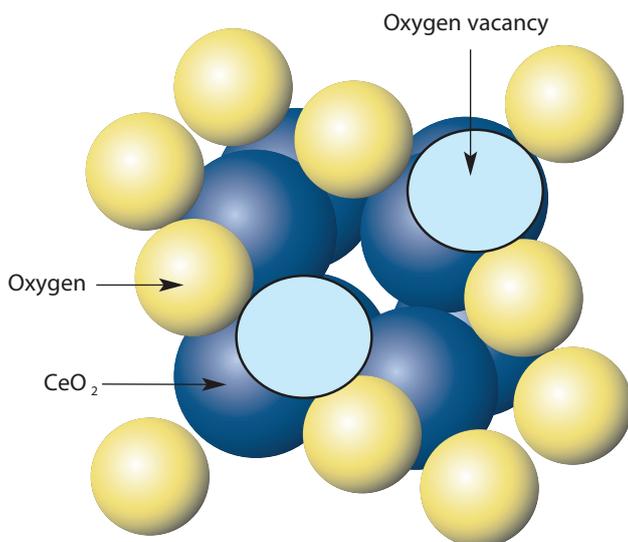
Catalysis

Catalytic Function of Cerium Oxide

Cerium oxide as a fuel additive

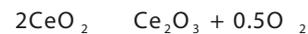
Cerium is a common naturally occurring element and is characterised chemically by having two valence states, +3 and +4. The +4 state is the only non-trivalent rare earth ion which is stable in an aqueous environment. It is, therefore a strong oxidising agent. The +3 state closely resembles the other trivalent rare earths.

There are numerous commercial applications for cerium including metallurgy, glass and glass polishing, ceramics, phosphors and catalysts. In catalysis, cerium is used in the form of cerium (IV) oxide, CeO₂. Cerium oxide is a highly stable, nontoxic, refractory ceramic material with a melting point of 2600°C and a density of 7.13 g.cm⁻³. The crystal structure is fluorite face centred cubic with a lattice constant of 5.11Å⁻¹. The rare earth oxides are generally some of the most thermally stable of all known materials and as such may be used in extremely high temperature applications without decomposition of the oxide².



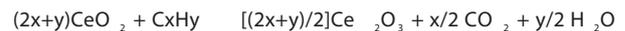
Fluorite structure of CeO₂ present in Envirox™

The efficacy of cerium oxide as a catalyst is related to its ability to undergo a transformation from the stoichiometric CeO₂ (+4) state to the Ce₂O₃ (+3) valence state via a relatively (at least in comparison with other oxides) low energy reaction. This is in turn related to the general property of fluorite oxide structures to deviate strongly from stoichiometry. Even at a loss of considerable amounts of oxygen from the crystal lattice, and the formation of a large number of oxygen vacancies as a result, the fluorite structure is retained. Such sub-oxides may readily be reoxidised to CeO₂ in an oxidising environment. Because no crystal structure phase change is involved in the supply and re-absorption of oxygen from the CeO₂ lattice, CeO₂ may be used as an oxygen storage material in catalysis via the following reaction³.



Cerium oxide has found an important application in exhaust three-way catalytic converters where harmful emissions from fuel burning are converted to harmless gases by the following series of reactions.

Hydrocarbon combustion:



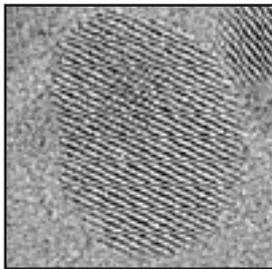
Soot burning:



NO_x reduction:



Unburnt fuel, particulates and harmful gases are reduced when cerium oxide is used as an exhaust catalyst⁴.



CeO₂ particle at a magnification of x6 million

In order for a catalyst to be effective when added into fuel three principal properties are required. Firstly, complete hydrocarbon oxidation should be promoted, secondly formation of NO_x should not be favoured, and finally the catalyst should remain thermally stable^{-5,6}.

As has been discussed, the ability of cerium oxide to donate oxygen allows complete hydrocarbon and soot burning in principle. In practice the activation energy of the cerium oxide, i.e. the lowest temperature at which oxygen donation occurs, is a crucial factor. Although the gas temperature of a diesel flame front is high (approximately 1700°C)⁷, a low catalyst 'switch-on' temperature will clearly promote a more complete fuel burn in the milliseconds during which combustion occurs⁸. A lower overall burn temperature, notwithstanding transient higher maximum temperatures, also mitigates against NO_x production due to the high activation energy of nitrogen oxidation⁹.

It has been demonstrated that the catalytic activity of cerium oxide is strongly dependent on particle size and surface area. The carbon combustion activation temperature is reduced from approximately 700°C for micron sized material to 300°C as the surface area of the material is increased by a factor of 20⁸. Oxygen vacancy atomic point defects are formed more easily on the surface of cerium oxide than in the bulk material and hence high surface area material has a substantially higher catalytic activity than bulk¹⁰. A high surface area is the key factor which allows ceramic based catalyst systems to compete with metals such as platinum or palladium as combustion catalysts.

The high thermal stability of cerium oxide results in Ce₂O₃ nanoparticles re-oxidising and remaining active after enhancing the initial combustion cycle. In a diesel engine

a significant amount of soot is formed and this may adhere to the internal combustion chamber surfaces as a deposit together with the lubricating oil mist. These deposits in turn affect the operation of the engine by introducing friction losses and variations in the internal surface heat loss behaviour¹¹. Although the piston head and chamber walls are comparatively cool in respect to the combustion flame the temperature still oscillates between 200°C and 500°C¹². This is exactly the range in which the nanoparticle cerium oxide carbon activation temperature lies and hence carbon deposits are gradually oxidised and removed from the engine allowing more efficient operation and reduced fuel consumption.

In conclusion, cerium oxide nanoparticles may be added to fuel and improve performance by promoting clean fuel and soot burn within the combustion cycle, and by gradually oxidising carbon deposit build within the engine resulting in more efficient performance and improved fuel economy.

References

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