

Potential rare-earth modified CeO₂ catalysts for diesel soot oxidation

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Introduction

Un-catalysed diesel soot (carbon particles) oxidation to CO₂ with a typical diesel engine exhaust gas (having H₂O, NO_x (NO+NO₂), hydrocarbons (HC), CO, and SO₂) generally occurs around 600°C [1]. When the diesel engine is fitted with an un-catalysed particulate trap frequently high temperature regenerations are required, which can be uncontrolled, inefficient, and uneconomic. On the other hand catalytic soot filter can utilise some of the exhaust gas/catalyst components to oxidise soot at much lower temperatures (around 400°C). A limited decrease in soot oxidation temperature can be observed in the presence of oxygen with SO₂ and H₂O and a significant decrease is reported with NO_x and lattice oxygen (of catalysts such as CeO₂). Even though lattice oxygen has comparable reactivity to that of NO₂ (NO₂ is generated from NO oxidation over catalyst) towards soot due to poor catalyst-soot contact lattice oxygen cannot be efficiently utilised. Furthermore, decreasing concentration of NO in the exhaust gases of modern diesel engines demands high rates of NO conversion to NO₂ and even multi-cycle oxidation for efficient soot oxidation. Pt and CeO₂ (ceria) are the major components in catalytic soot filters, whose function is to convert NO to NO₂ and also provide the lattice oxygen. From the studies so far, the textural and redox properties of the support in providing lattice oxygen/adsorbed oxygen to soot or NO (to generate NO₂) are not obvious. In this presentation the role of surface and bulk active species in soot oxidation via lattice oxygen and by NO conversion to NO₂ will be elucidated. Various successful strategies can be followed to increase such active species. This will lead to rare earth doped ceria catalysts that significantly decrease soot oxidation temperature with O₂ and NO+O₂.

Results and Discussion

CeO₂ and rare-earth (La, Pr, Sm, and Y) doped CeO₂ catalysts with and without Pt are prepared and soot oxidation under tight contact and realistic loose contact conditions are studied with O₂ and NO+O₂. The catalysts are characterised by XRD, H₂-TPR, DRIFTS, and Raman spectroscopy. With oxygen alone as an oxidant, under realistic catalyst-soot loose contact conditions a small decrease in soot oxidation temperatures is observed (around 25°C). With tight contact catalyst-soot mixtures oxidation temperature can be decreased by about 150°C. Praseodymium and lanthanum doped CeO₂ show the best soot oxidation activity with O₂. In the presence of NO+O₂, NO conversion to NO₂ over the catalysts governs the soot oxidation activity and it is found that CeO₂ lattice oxygen participates in NO conversion to NO₂. Praseodymium is the best dopant, which decreased soot oxidation temperature by about 150°C with NO+O₂ in loose contact mode (Fig. 1).

Doping CeO₂ with rare-earth ions will: 1) increase the external surface area, 2) create oxygen vacancies (Fig. 2), and 3) increase loosely bound lattice oxygen (decreases in surface and bulk reduction temperature). Different dopants change the surface and redox properties to different extents and bulk reduction in general takes place above 500°C. Therefore, bulk lattice oxygen involvement in soot oxidation with O₂ or NO conversion to NO₂ is very limited below 500°C, if any. Soot oxidation with O₂ correlated well with the

improvement in external surface area. The ease of surface reduction has relatively weaker correlation.

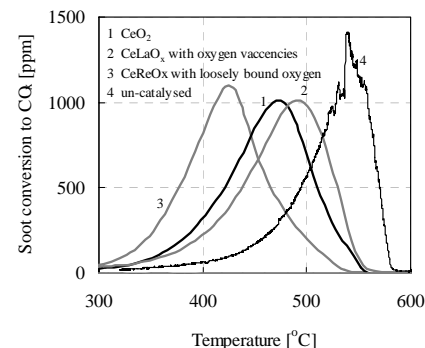


Fig. 1 Soot oxidation over CeO₂ and CeReOx catalysts with NO+O₂ under loose contact.

Therefore, Pr shows superior soot oxidation activity, among the catalyst formulations tested. Based on the experimental results it is suggested that for realising increase in the soot oxidation rate with O₂ under realistic loose contact conditions, the catalyst external surface area should be increased. On the other hand all catalyst surface is accessible for NO conversion to NO₂. The soot conversion with NO+O₂ over lanthanum doped CeO₂ (15 m²g⁻¹) is, however, not significantly different, compared with CeO₂ (2 m²g⁻¹), Fig. 1. Furthermore, non-reducible dopants such as lanthanum leads to decrease in the surface oxygen density by creating vacancies, whereas reducible ions such as praseodymium increases the surface oxygen density by creating loosely bound oxygen. Over praseodymium doped ceria the loosely bound oxygen can be easily transferred to NO generating NO₂ needed for soot oxidation under loose contact conditions, leading to superior catalyst. From the new insights obtained the design of praseodymium modified CeO₂ catalysts will lead to soot oxidation activity comparably to that of Pt catalysts in the presence of NO_x.

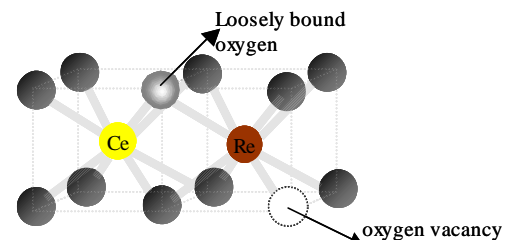


Fig. 2 Structure of rare-earth modified CeO₂

The oxygen vacancies have no positive influence on soot oxidation. Praseodymium doping significantly increases the external surface area and easily reducible surface ions, *i.e.* surface that easily loses oxygen to soot and, therefore, shows superior soot oxidation activity, among the catalyst formulations tested. Based on the experimental results it is suggested that for realising increase in the soot oxidation rate with O₂ under realistic loose contact conditions, the catalyst external surface area should be increased. The oxygen vacancies have no positive influence on soot oxidation. Praseodymium doping significantly increases the external surface area and easily reducible surface ions.

Reference:

B.A.A.L. van Setten, M. Makkee, and J.A. Moulijn, Catal. Reviews 43 (2001) 489.