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Enhanced soot oxidation by lattice oxygen via La^{3+}-doped CeO_2

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Abstract

The catalytic behaviours of CeO_2 and a series of La^{3+}-doped CeO_2 catalysts (La^{3+} loading between 5 and 50 wt%) have been studied for soot oxidation by O_2. XRD and Raman spectroscopy characterisation indicated that solid solutions are formed in the studied Ce/La ratio, in which La^{3+} cations replace Ce^{4+} cations in the CeO_2 lattice. Thermogravimetric analysis showed that La^{3+} significantly improves CeO_2 catalytic activity for soot oxidation with O_2. The best catalytic activity was found with 5 wt% La^{3+}-doped CeO_2 catalyst (CeO_2-5La), in both loose and tight contact conditions. This improvement seems to be related to the increase in BET surface area and the change in the catalyst redox properties of CeO_2 brought about by doping with La^{3+}. La^{3+} decreases the onset temperature of Ce^{4+} to Ce^{3+} reduction by H_2 from 580 °C (CeO_2) to 325 °C (CeO_2-5La) and increases the amount of Ce^{4+} that can be reduced by H_2 (maximum amount for CeO_2-5La catalyst).

An advanced TAP reactor is used for the first time to study catalysed soot oxidation with labelled oxygen. In the absence of catalyst, oxidation starts above 500 °C, and mainly labelled oxidation species (CO and CO_2) were found. In the presence of catalyst, it is shown that the gas-phase labelled oxygen replaces nonlabelled lattice oxygen, creating the highly active nonlabelled oxygen. This highly active nonlabelled oxygen reacts with soot, giving CO and CO_2. The creation of such active oxygen species starts from 400 °C and thereby decreases the soot oxidation temperature. CeO_2-5La produces more such active species, for example, leading to 98% oxygen conversion at 400 °C compared with 37% over CeO_2 alone under identical circumstances.

Keywords: Active oxygen; Catalysed soot oxidation; Ceria; Lanthana; Oxygen exchange; Solid solution; Soot; Temporal analysis of products

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1. Introduction

Air quality is an environmental problem that must be tackled by today's society [1]. Although the quality of air in urban areas is improving, in spite of growing urbanisation, because of increasing human mobility and, therefore, the increasing number of vehicles in our cities, still further improvement is needed.

The most used internal combustion engines in vehicles are the Otto and Diesel engines. The combustion processes occurring in these engines are almost 100% complete. However, some undesirable by-products are formed. Otto engines, running on gasoline, generate mainly CO, hydrocarbons (HC), and NO_x, whereas diesel engines produce small-size carbon particles (soot), NO_x, and small amounts of CO and HC.

Diesel exhaust gases had traditionally been considered clean in comparison with the exhaust gases of gasoline vehicles [2], but the successful introduction of three-way catalyst (TWC) for use in gasoline-powered vehicles and the development of modern engines have changed this benefit of diesel engines. Therefore, the search for particulate and NO_x reduction techniques is an issue of current scientific and technological research.

The conventional TWC used in gasoline engines converts simultaneously the HC, CO, and NO_x present in the exhaust gas into H_2O, CO_2, and N_2. Typical TWC formulations combine very active noble metals such Pd, Rh, or Pt on an oxygen storage component, generally based on rare earth oxides [3]. The optimal performance of these catalysts

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is reached when the exhaust gas is present in a stoichiometric air/fuel ratio (14.6:1). However, the gas composition oscillates slightly around this ratio, and the buffer properties of the rare earth component permit the storage of oxygen during fuel-poor periods (net oxidising) and supply additional oxygen during fuel-rich periods (net reducing). Automotive pollution control is the most important application of rare earth oxides today [4]. The main properties of rare earth oxides for this TWC application are (i) a large oxygen storage capacity via the redox process $Ce^{4+} \leftrightarrow Ce^{3+}$; (ii) improvement of noble metals dispersion; (iii) improvement of the thermal stability of supports; and (iv) promotion of the water–gas shift reaction [5].

A catalytic device like TWC is not available for NO_x and soot elimination in diesel exhaust gases, in spite of the great advances that have been made in the last years in diesel particulate-trapping techniques [6]. Because of the lean-burn conditions in the diesel engine, NO_x reduction can only be performed via selective catalytic reduction with urea or hydrocarbon as a reductant. The main problem of soot elimination is that the onset temperature for soot combustion catalysts ($> 500\,°C$) is too high for spontaneous regeneration of the filters, and, therefore, it is necessary to ignite soot periodically by raising the temperature with or without diesel fuel addition [7]. This technology is commercially available for soot abatement. Another technical approach is the oxidation of soot with NO_2 (NO_2 is converted from NO), which is much more reactive than O_2 [6,8]. Strategies for the reutilisation of NO in several cycles have also been developed [9]. Recently it has been found that CeO_2 has the potential to increase the oxidation rate of soot, because of the creation of “active oxygen” [10]. This finding opens a new route for the development of soot oxidation catalysts based on these species. The generation and feasible utilisation of highly reactive “active oxygen” for soot oxidation is a focus of ongoing investigation.

Despite the fact that CeO_2 and CeO_2-based solid solutions containing different rare earth metals have been extensively studied for TWC application [3,4], few detailed studies have analysed the utilisation of these materials for soot oxidation [11,12].

In this study, La^{3+}-doped CeO_2 catalysts have been prepared and tested for soot oxidation, and their activity has been compared with that of CeO_2. In this paper we present results for (i) the preparation of La^{3+}-containing CeO_2 solid solutions with different Ce/La ratios; (ii) the catalytic activity of these materials for soot oxidation by O_2; (iii) the characterisation of the crystalline structure, surface area, and redox properties of these materials, which will provide information about the key factors that control the catalytic activity of these materials for soot oxidation; and (iv) study of the interaction of O_2 with catalysts and soot-catalyst mixtures in an advanced TAP reactor with the use of normal and labelled O_2, which provides information about the role of “active oxygen” species in the O_2 soot oxidation reaction.

2. Experimental

2.1. Catalyst preparation

Nine catalysts have been prepared, one pure CeO_2 catalyst and eight La^{3+}-containing CeO_2 catalysts. La^{3+}-containing catalysts were denoted as CeO_2-%La, where % stands for the target La^{3+} percentage, determined by the formula $\% = (100 \cdot g_{La})/(g_{Ce} + g_{La})$. The CeO_2 catalyst was denoted as CeO_2.

$Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich, 99%) and $La(NO_3)_3 \cdot 6H_2O$ (Merck, 99%) were used as precursors for catalyst preparation. The required amounts of these precursors were physically mixed in a mortar and were thermally treated in a furnace at 1000 °C for 90 min in air (heating rate 10 °C/min).

2.2. Characterisation

The BET surface areas of catalysts were determined by physical adsorption of N_2 at $-196\,°C$ in an automatic volumetric system (Autosorb-6, Quantachrome).

Temperature-programmed reduction by H_2 (TPR) was carried out in a tubular quartz reactor (inner diameter 5 mm) coupled to a TCD analyser for monitoring H_2 consumed. In the experiments the sample (50 mg of fresh catalyst) was heated at 10 °C/min from room temperature to 1000 °C in 30 ml/min flow of 7.7 vol% H_2 in Ar. To quantify the total amount of H_2 consumed during the experiments, CuO was used as a calibration reference.

Raman spectra were recorded in a Renishaw Raman imaging microscope (system 2000) with a 20-mW Ar laser (514 nm). The Raman microscope was calibrated with the use of a silicon wafer.

X-ray diffractograms were recorded with a Philips X-ray diffractometer (PW 1840) using Ni-filtered Cu-K_α radiation ($\lambda = 0.15418$ nm).

Temporal analysis of products (TAP) was used to analyse the interaction between gas-phase O_2 and selected catalysts (CeO_2 and CeO_2-5La) at temperatures between 200 and 600 °C in the so-called Multitrack system, with labelled and nonlabelled oxygen. A small cylindrical reactor (7 mm i.d.) containing the catalyst was connected to an ultrahigh vacuum system (10^{-6} Pa). Small gas pulses, typically consisting of $\sim 10^{16}$ molecules of pure oxygen, were fed to the catalyst with high-speed gas pulsing valves. The reactor was coupled to three mass spectrometers that were able to measure the components of the gas leaving the reactor with a maximum sampling frequency of 1 MHz. In a separate experiment Ar gas was pulsed through the catalyst bed at different temperatures, and it can be assumed that it did not interact chemically with the catalyst. Therefore, the Ar response profile is a reference for noninteracting gas. Comparison of the Ar and O_2 responses shows the extent of the interaction. The oxygen pulse experiments were carried out with 100 mg of catalyst (around 10^{20} molecules of CeO_2), and this amount is much higher than the amount of gas molecules pulsed. At