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Structural characterisation of $Ce_{0.5}Zr_{0.5}O_2$ modified by redox treatments and evaluation for chlorinated VOC oxidation

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ABSTRACT

In this work the application of a redox treatment consisting of a high-temperature reduction with 5%H_2/Ar in the range 950–1075 °C for 0.5–3 h followed by mild oxidation at 550 °C with 5%O_2/He was evaluated as a tool for improving the catalytic performance of $Ce_{0.5}Zr_{0.5}O_2$ mixed oxide in the combustion of chlorinated compounds. Structural, morphological and physico-chemical changes caused by the redox treatment were analysed by X-ray diffraction, Raman spectroscopy, BET measurements, NH_3-temperature programmed desorption, temperature programmed reduction with hydrogen, and oxygen chemisorption. Interestingly, after reduction at a temperature as high as 1050 °C during at least 1.5 h, a substantially enhanced redox behaviour was noticed which resulted in a significant promotion of the catalytic activity in comparison with the unmodified parent sample. Hence, the value of temperature of half conversion at 30,000 h^{-1} decreased from 300 to 275 °C for the combustion of 1,2-dichloroethane, which was selected as a model chlorinated feed. This active performance was assigned to the formation of a new κ-$CeZrO_4$ phase after redox aging characterised by a markedly increased capacity of providing active oxygen species at low temperatures. For comparative purposes two additional $Ce_{0.5}Zr_{0.5}O_2$ samples calcined at 750 and 1000 °C were also characterised and catalytically tested.

1. Introduction

The release of volatile organic compounds (VOCs) to the atmosphere results in tangible environmental damage. These pollutants can contribute to atmospheric processes which can have detrimental effects on human health. For example, VOCs have been implicated in the formation of ground level ozone, ozone depletion and often they act as greenhouse gases. In September 2005, the Commission of the European Communities in the Framework of the "Clean Air For Europe" (CAFE) Programme published its Thematic Strategy on Air Pollution [1]. This strategy sets health and environmental objectives and emission reduction targets for the main pollutants. More specifically, its aim is to cut the annual number of premature deaths caused by air pollution by 40% by 2020 from the 2000 level and to reduce the continuing damage to Europe's ecosystems. To achieve these objectives, emissions of sulphur dioxide will need to be reduced by 82%, nitrogen oxides by 60%, volatile organic compounds by 51%, ammonia by 27% and fine particulate matter by 59% (compared to their 2000 levels).

VOCs are wide ranging in chemical functionality and their emission sources (off-gases from chemical plants, groundwater decontamination by air stripping, odour emission control, and contaminated air in solvent evaporation processes), but it is clear that chlorohydrocarbons are some of the most difficult to abate by catalytic combustion. Chlorinated compounds require a special attention on account of their toxicity, high stability and widespread application in industry [2]. Consequently, the discovery of efficient novel catalysts for low-temperature complete destruction of chlorinated VOCs is a challenging task of ongoing interest [3]. 1,2-Dichloroethane (DCE) or ethylene dichloride ($C_2H_4Cl_2$) is probably one of the most important chlorinated VOC emitted in gaseous industrial waste streams. It is used as an intermediate for the production of polyvinyl chloride (PVC), the most produced plastic in the world (17.5 million tons per year in USA, Europe and Japan) after polyethylene. Vinyl chloride or chloroethene (C_2H_3Cl) is the monomer of PVC and industrially prepared from ethylene and chlorine [4]. Ethylene is converted into DCE via oxychlorination and direct chlorination at 200–300 °C. DCE is then thermally cracked into vinyl chloride. Overall the reactions are performed at relatively high selectivity (>98%) but the scale of the process results in the formation of significant quantities of chlorinated C_1 and C_2 by-products, and unconverted DCE. Approximately 80% of the world's consumption of 1,2-dichloroethane is applied to the production of vinyl chloride monomer. Less important uses are as a solvent in textile cleaning and metal degreasing and paint remover, a starting material for paint, varnish, and finish removers, a cleaner for

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upholstery and carpets, a fumigant, a lead scavenger in antiknock gasoline, and as a dispersant for plastics and elastomers such as synthetic rubber [5].

Ceria–zirconia mixed oxides continue to attract considerable attention because of their current and potential use in catalytic applications: as electrolyte materials for solid oxide fuel cells [6,7]; as supports in catalysts for the generation and purification of H_2 [8,9]; but most notably for their use in automotive three-way catalysts [10,11], in which these oxides are included as a standard component to promote the oxygen storage capacity of the catalyst. Other environmental applications include CO oxidation, light hydrocarbons combustion and soot removal. The key to their catalytic activities is the ability of Ce^{4+} to be reversibly reduced to Ce^{3+} at moderate temperatures. This property is associated with considerable oxide-ion mobility in the solid state from surface to bulk and vice versa.

Previous studies carried out in our research group have shown promising results of the use of Ce/Zr mixed oxides for chlorinated VOCs oxidative decomposition [12,13]. In a comparative study among several samples with varying Ce/Zr ratio for DCE abatement $Ce_{0.5}Zr_{0.5}O_2$ proved to be significantly superior to the others by producing over 95% conversion at temperatures of about 400 °C. This sample also resulted markedly active for the removal of other chlorinated compounds such as trichloroethylene. The catalytic combustion is believed to chiefly involve redox catalysis with surface acidity playing a relevant catalytic role as well. Other attractive features of Ce/Zr mixed oxides are that they do not favour the formation of coke deposits, and exhibit a reasonable chemical stability preserving their catalytic performance after severe chlorine-poisoning [14].

The catalytic behaviour of these mixed oxides depends not only on the composition or the synthesis route but also on the previous redox history, which provides a tool for tuning the redox behaviour. In particular, high-temperature reduction treatments are found to favour the formation of highly active materials with very desirable low-temperature redox properties [15,16]. In this work the impact of induced redox aging on the catalytic behaviour of $Ce_{0.5}Zr_{0.5}O_2$ was examined for the gas-phase catalytic destruction of chlorinated volatile organic compounds. A characterisation study was undertaken to investigate the nature of the changes provoked. The comparative performance of fresh (calcined in air at 550 °C) and redox aged (reduced at 950–1075 °C for 0.5–3 h with $5\%H_2/Ar$ followed by mild oxidation at 550 °C with $5\%O_2/He$ for 0.5 h) samples was assessed using the oxidative destruction of 1,2-dichloroethane, which is a common chlorinated pollutant found in many commercial waste streams, in a fixed-bed flow reactor.

2. Experimental

2.1. Catalyst preparation

The original $Ce_{0.5}Zr_{0.5}O_2$ sample was synthesised by Rhodia using a proprietary coprecipitation method (precipitation route from nitrate precursors) [17]. This sample was stabilised by calcination in air at 550 °C for 4 h in a muffle furnace (fresh sample denoted as O550-4). The oxide was then submitted to redox aging at high temperature. The process consisted of a reduction step under flowing $5\%H_2/Ar$ ($50\,cm^3\,min^{-1}$) at temperatures in the 950–1075 °C range for 0.5, 1.5 and 3 h. After cooling in a flow of helium ($50\,cm^3\,min^{-1}$) down to 550 °C the sample was reoxidised under flowing oxygen ($5\%O_2/He$, $50\,cm^3\,min^{-1}$) for 0.5 h (redox aged samples or samples H). The redox treatment is schematically depicted in Fig. 1. As an example of the labelling code used, the sample H1075-3 corresponds to a sample submitted to a reduction step with hydrogen at 1075 °C for 3 h. For comparative purposes two additional $Ce_{0.5}Zr_{0.5}O_2$ samples were obtained by calcination in air for 4 h at 700 and 1000 °C, denoted as O700-4 and O1000-4, respectively (oxidised samples or samples O). Catalyst pellets with diameter from 0.3 to 0.5 mm were prepared by compressing the oxide powders into flakes in a hydraulic press (Specac), followed by crushing and sieving. Fresh and thermally treated samples, before they were subjected to catalytic activity and selectivity experiments, were characterised using several analytical techniques.

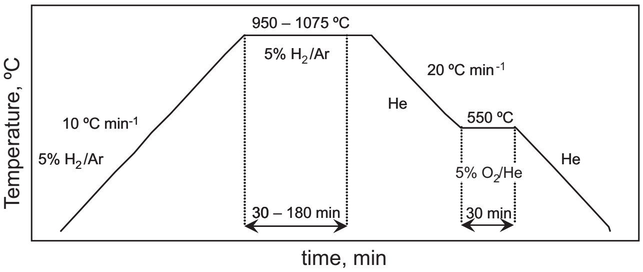

Fig. 1. Schematic diagram of the temperature–time patterns for redox aged $Ce_{0.5}Zr_{0.5}O_2$ samples.

2.2. Characterisation techniques

Textural properties were evaluated from the nitrogen adsorption–desorption isotherms, determined at −196 °C with a Micromeritics ASAP 2010 apparatus. The specific areas of the samples were determined according to the standard BET procedure using nitrogen adsorption taken in the relative equilibrium pressure interval of 0.03–0.3. Mean pore size was calculated from the BJH method. The samples were previously degassed overnight at 300 °C under high vacuum. X-ray diffraction (XRD) studies were carried out on a X'PERT-MPD X-ray diffractometer with CuKα radiation ($\lambda = 1.5406$ Å) and Ni filter. The X-ray tube was operated at 30 kV and 20 mA. Samples were scanned from $2° < 2\theta < 80°$ and the X-ray diffraction line positions were determined with a step size of 0.02° and a counting time of 2.5 s per step. Phase identification was carried out by comparison with JCPDF database cards.

Raman spectra were recorded with a Renishaw InVia Raman spectrometer coupled to a Leica DMLM microscope. The spectra were acquired with a Leica 50x N Plan (0.75 aperture) objective. Besides Leica 5x N Plan (0.12 aperture) and 20x N Plan (0.40 aperture) objectives were used for visualisation and focusing. The spatial resolution for the 50× objective was 2 μm. For focusing and searching of the points of interest, the microscope implemented a Prior Scientific motorised stage (XYZ) with a joystick. The spectrometer was equipped with a 514 nm laser (ion-argon laser, Modu-Laser) with a nominal power at the source of 50 mW, being the maximum power at the sample of 20 mW. A holographic net of 1800 lines/mm was used. In all measurements, the power of the laser was reduced in order to avoid the photo-decomposition of the samples (burning) by using neutral density filters. For each spectrum 10 s were employed and 20 scans were accumulated with the 10% of the maximum power in the spectral window from 100 to $800\,cm^{-1}$.

Temperature-programmed desorption (TPD) of ammonia was performed on a Micromeritics AutoChem 2920 instrument equipped with a quartz U-tube coupled to a thermal conductivity detector. Prior to adsorption experiments, the samples (30 mg) were first pre-treated in a $5\%O_2/He$ stream at 550 °C. Then, they were cooled down to 100 °C in a He flow ($20\,cm^3\,min^{-1}$). Later, the NH_3 adsorption step was performed by admitting a flow of $10\%NH_3/He$ at 100 °C up to saturation. Subsequently, the samples were exposed to a flow of helium ($50\,cm^3\,min^{-1}$) for 2 h at 100 °C