



Influence of the preparation method on the activity of ceria zirconia mixed oxides for naphthalene total oxidation

David R. Sellick^a, Asunción Aranda^b, Tomas García^b, José M. López^b, Benjamín Solsona^c, Ana M. Mastral^b, David J. Morgan^a, Albert F. Carley^a, Stuart H. Taylor^{a,*}

^a Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK

^b Instituto de Carboquímica (CSIC), C/Miguel Luesma, 50018 Zaragoza, Spain

^c Departament d'Enginyeria Química, Universitat de València, C/Dr. Moliner 50, 46100 Burjassot, Valencia, Spain

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ABSTRACT

Cerium/zirconium mixed oxides, with different Ce/Zr ratios, have been synthesised by a co-precipitation method using two different precipitating agents (sodium carbonate and urea) and tested for the total oxidation of naphthalene. Catalysts were characterised by N₂ adsorption, XRD, Raman, TPR, XPS and DRIFTS. Ceria prepared by carbonate precipitation had low activity and this is likely to be related to the high concentration of residual surface carbonate that covers catalytic sites and inhibits reaction. For carbonate precipitation, increasing the Zr content to 1% resulted in a significant increase of activity, which is related to the decrease of surface carbonate. Increasing the Zr content up to 50% resulted in catalysts more active than ceria, but activity decreased as Zr content increased. This was in spite of increasing the number of oxygen vacancies, and this effect has been related to the decrease in the number of surface hydroxyl groups, which favours naphthalene adsorption. Ceria prepared by urea precipitation was markedly more active than that produced by carbonate precipitation. The urea-derived catalyst with 1% Zr is marginally more active than pure ceria, whilst for higher Zr contents activity was marginally lower. Two factors can account for these observations; they are the increase of oxygen vacancies contributing positively to activity and the opposing negative effect of decreasing the number of surface hydroxyl groups when the zirconium content increases.

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1. Introduction

Naphthalene is a Polycyclic Aromatic Hydrocarbon (PAH), which is a specific group of pollutants classified within a wider group of pollutants known as Volatile Organic Compounds (VOCs). VOCs are now recognised as serious atmospheric pollutants [1]. Due to the more recent public and political attitudes towards atmospheric pollution, several legislative measures have been implemented to control VOC emissions. An example was the Gothenburg Protocol of 1999, which stated that VOC emissions needed to be reduced by at least 40% by 2010. VOCs are responsible for causing some illnesses [2], and they have also been implicated in the formation of ground level ozone [1] and photochemical smog [2].

Naphthalene has been detected as a waste product in many commercial and domestic applications, such as emissions from diesel exhaust [3]. Of the methods available for the removal of naphthalene, catalytic oxidation is the most efficient in terms of monetary cost and energy efficiency. For example, thermal incineration is an

option, but much higher treatment temperatures are required. It is also undesirable as the high temperatures can lead to the formation of nitrogen oxides (NO_x) and other toxic by-products, such as dioxins and dibenzofurans, if the process is not carefully controlled.

The catalytic total oxidation of PAHs has not been studied extensively when compared with other VOCs, but there are a number of reports describing the use of a range of catalysts [4]. Naphthalene has been commonly used as a suitable model PAH, and precious metal based catalysts (particularly Pd and Pt) are consistently active on a variety of supports. Zhang et al. reported that Pd and Pt catalysts supported on γ -Al₂O₃ were very active compared to other transition metals, such as W and Co [5]. The modification of 0.5 wt% Pt/ γ -Al₂O₃ by 0.5 wt% vanadium was reported by Ndifor et al. [6] to improve activity; however, higher V loadings had a detrimental effect on activity due to the formation of crystalline V₂O₅.

In recent years, nanocrystalline ceria has been identified as being one of the most active catalysts for the total oxidation of naphthalene [7]. Previous studies have focussed on the influence of ceria preparation variables, with the aim of determining which catalyst features are required for naphthalene total oxidation. Factors such as crystallite size, surface area and oxygen defect concentration were all identified as having an important controlling influence

* Corresponding author.

E-mail address: taylorsh@cardiff.ac.uk (S.H. Taylor).

[7,8]. Hence, the addition of platinum nanoparticles onto the surface of nanocrystalline ceria would be expected to improve the activity further. However, a recent study shows that adding platinum suppresses the activity when compared to ceria alone [9], and the same type of behaviour has also been observed for the addition of gold nanoparticles [10]. Therefore, a driving force to identify more active catalysts for PAH abatement exists, but it appears that the addition of precious metal nanoparticles to the active high surface area ceria is not an effective approach. Recently, we have found that copper doped ceria catalysts, where copper was fully incorporated into the ceria lattice, have better performance when compared to precious metal based catalysts [11]. For these catalysts, it was demonstrated that the surface oxygen defects were important for controlling naphthalene oxidation, since the addition of very low amounts of copper to non-ordered mesoporous ceria promotes the activity and selectivity to produce a very active catalyst for naphthalene total oxidation. Increasing the amount of oxygen defects has also been reported for the introduction of a range of other ions into the CeO_2 lattice [12], and the incorporation of Zr^{4+} ions is one of the most studied catalytic systems due to their extended use in vehicle exhaust after-treatment catalysts [13,14]. Accordingly, it has been reported recently that the addition of zirconium into the lattice of ceria improves the activity for naphthalene total oxidation [15], the catalytic activity for naphthalene oxidation over CeO_2 - ZrO_2 mixed oxide catalysts being directly related to the catalyst redox properties. The sequence of reducibility of the catalysts followed the order: $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2 > \text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2 > \text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$, which was the same order as the catalytic activity. Therefore, it is of interest to know if incorporation of lower amounts of Zr^{4+} into the ceria lattice could lead to improved catalyst performance for PAH oxidation. Thus, the aim of the present study is to investigate the role of zirconium addition on a range of zirconia doped ceria catalysts prepared by coprecipitation and used for the catalytic combustion of naphthalene. Furthermore, we have investigated the influence of preparation route, and a comparison has been made of catalysts prepared by coprecipitation using urea and those precipitated with sodium carbonate.

2. Experimental

2.1. Catalyst preparation

The cerium/zirconium mixed oxides were synthesised using two different precipitation methods – one used urea as the precipitating agent and the other sodium carbonate. $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (Aldrich) was used as the cerium source and $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (Aldrich) was used as the zirconium source. The two series of catalysts were prepared with Ce/Zr molar ratios of 100/0, 99/1, 90/10, 80/20 and 50/50. The sample identifiers for the catalyst series are prefixed with U- or C-, which denotes precipitation using urea and carbonate respectively, and of the format $\text{CeZrO}_x\text{-a/b}$, where a and b relate to the molar percentage of cerium and zirconium respectively.

For the urea precipitated catalysts, urea (Aldrich, ACS reagent, 99–100.5%, 40 g), distilled water (200 mL) and the appropriate amounts of ammonium cerium(IV) nitrate (Aldrich, 99.99+ %) and zirconyl nitrate hydrate (Aldrich, 99%) were aged under reflux conditions with stirring in a round-bottomed flask for 24 h at 100 °C in the pH range 8–9. The resulting slurry was filtered, washed with deionised water and dried at 110 °C overnight. This was followed by calcination in static air at 500 °C for 6 h with a ramp rate of 10 °C min⁻¹. For the carbonate precipitated catalysts, 0.25 M solutions of zirconyl nitrate hydrate (Aldrich, 99%) and ammonium cerium(IV) nitrate (Aldrich, 99.99+ %), in proportions dependent

on the desired Ce/Zr ratio, were combined and heated to 80 °C with stirring. Aqueous sodium carbonate solution (0.25 M) was then added dropwise until a pH of 8–9 was reached. This was then aged at 80 °C with stirring for 1 h. The precipitate was filtered, washed with distilled water and then dried at 110 °C overnight. The dried precursors were calcined for 3 h at 400 °C in static air with a ramp rate of 10 °C min⁻¹.

2.2. Catalyst characterisation

Surface areas were determined using the BET method and were performed using a Micromeritics Gemini 2360 instrument. The catalysts were degassed under an N_2 flow at 120 °C for 45 min prior to performing a five point analysis at –196 °C.

Powder X-ray diffraction (XRD) patterns were obtained using a PANalytical X'pert Pro diffractometer equipped with a Cu K α X-ray source. Conditions of 40 kV and a current of 40 mA were used. Data were collected over the angular range of 10–80° 2 θ . Crystalite sizes were calculated using the Scherrer method, by comparing the FWHM of diffraction peaks against a highly crystalline silicon standard.

Laser Raman spectra were obtained using a Renishaw Ramascope fitted with a Spectraphysics argon ion laser ($\lambda = 514$ nm) at a power of 20 mW. An Olympus BH2-UMA microscope was used for laser focussing. Scanning electron microscopy images were obtained using a Carl Zeiss EVO 40 scanning electron microscope fitted with backscattered and secondary electron detectors. For image collection using these detectors, variable working distances and probe currents were used. An EHT of 25 keV was used for all sample imaging, and samples were mounted on carbon adhesive discs. For energy dispersive X-ray (EDX) elemental analysis, the same microscope was used with a working distance of 9 mm and data was collected using an Oxford Instruments analyser.

Temperature programmed reduction (TPR) studies were carried out on a Micromeritics Autochem II 2920 with Cryocooler using 10% H_2 in Ar as the analyte gas, with a flow of 50 cm³ min⁻¹ over a temperature range of 50–800 °C. A sample mass of ca. 100 mg was used.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies were carried out with a VERTEX 70 FTIR instrument operated with OPUS software. A Spectratech DRIFT high-temperature cell was filled with the powdered sample. The required gas flow (synthetic air or naphthalene in N_2) of 25 cm³ min⁻¹ was maintained by mass-flow controllers. Moisture free catalyst spectra were obtained after heating the sample at 150 °C for 30 min. Prior to the *in situ* adsorption/reaction measurements by DRIFTS at 250 °C, the samples were activated at 400 °C for 30 min in synthetic air flow. Each spectrum presents an average of 32 scans collected with a spectral resolution of 2 cm⁻¹. The spectra shown were obtained after subtraction of the features from the catalyst, recorded at 250 °C in He. Below 750 cm⁻¹ the spectra showed specular reflections and, therefore, this region is not included in the discussion.

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD photoelectron spectrometer fitted with a monochromatic Al source (photon energy = 1486.6 eV). Pass energies of 40 eV (high resolution scans) and 160 eV (survey spectra) were used over an analysis area of 700 × 300 μm . All spectra were calibrated to the C(1s) binding energy for adventitious carbon (binding energy = 284.7 eV). XPS data were analysed using CasaXPS software. Shirley background subtraction was applied to all the raw data. All peaks of the corrected plot were fitted with a Gaussian–Lorentzian shape function to peak fit overlapping features. Iterations were performed using the Marquardt method. Standard deviations were always lower than 1.5%.

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