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The influence of cerium to urea preparation ratio of nanocrystalline ceria catalysts for the total oxidation of naphthalene

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Abstract

The influence of cerium salt/urea ratio on the activity of nanocrystalline ceria catalysts prepared by homogeneous precipitation with urea for the complete oxidation of naphthalene has been evaluated. Ceria catalysts were prepared from five different cerium salt/urea ratios (2:1, 1:1, 1:2, 1:3 and 1:4). Catalyst characterization (by BET, XRD and TPR) only revealed subtle differences in the characteristics of these catalysts with cerium salt to urea ratio. However, Raman and scanning electron microscopy (SEM) results indicated differences in the oxygen defect concentration (FWHM of Raman band) and morphology of the catalysts with variation of the preparation ratio. Catalysts prepared with 2:1, 1:1 and 1:4 were significantly more active than those prepared from 1:2 and 1:3 ratios. A relationship between the concentration of oxygen defects and naphthalene oxidation activity has been established. The activity of the catalysts is thought to be related to a combination of oxygen defect concentration, surface reducibility and morphology.

Keywords: Catalytic oxidation; Ceria; Naphthalene; PAHs; VOCs

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1. Introduction

Ceria is a material known to have versatile properties as a catalyst [1] and is certainly the most significant member of the oxides of rare earth elements in industrial catalysis [2]. Ceria has potential for applications in the removal of soot from diesel engine exhaust [3], catalytic waste oxidation for the removal of organics from waste waters [4], and as a component of combustion catalysts [5]. The ability of ceria to enhance the removal of CO, hydrocarbons (HCs) and NO_x makes it a critical component of the high-performance three-way catalyst for the treatment of automotive exhaust gases. The importance of CeO_2 in such systems originates mainly from the ability to act as an oxygen buffer, storing/releasing oxygen due to the Ce^{4+}/Ce^{3+} redox couple [6–8]. In addition to acting as an oxygen reservoir in the three-way catalyst, ceria stabilizes the alumina support and maintains a high surface area [9,10]; and it stabilizes the dispersed state of precious metals by preventing them from sintering [11,12] and promotes CO oxidation [13–15] and the water-gas shift reaction [16–18]. It is therefore clear that over the years, the catalytic behavior of ceria has attracted considerable investigation for a range of applications. With the ever increasing quest for pollution control and environmental protection, many studies have concentrated on developing ceria-based catalysts for VOC, CO and NO_x control [1–18].

Several synthetic methods have been used for the preparation of CeO_2 nanoparticles. These include hydrothermal [19,20], redox reaction [21], sonochemical [22], pyrolysis [23], reverse micelles [24] and homogeneous precipitation methods [25–27]. The mild synthetic conditions and relatively simple procedure involved in homogeneous precipitation give it an advantage over the other synthesis techniques. Garcia et al. [28,29] showed that a CeO_2 catalyst prepared by homogeneous precipitation with urea (CeO_2 (U)) was more effective than Pt/Al_2O_3 and other metal oxide catalysts reported for the total oxidation of naphthalene. Naphthalene is an atmospheric pollutant and a carcinogen, and it is an excellent model for the class of compounds known as polycyclic aromatic hydrocarbons (PAHs). In a recent study [30], we have shown that naphthalene total oxidation activity of a CeO_2 catalyst prepared

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in a similar manner as reported earlier [28] is dependent on the preparation variables, such as calcination temperature, calcination time and aging time. Variation of these conditions altered the surface area, crystallite size, oxygen defect concentration, surface reducibility and morphology of this CeO_2 (U) catalyst, and hence influenced activity [30]. It is also probable that the ratio of the cerium salt to urea in the precipitation process would also affect the chemical and structural properties of the catalyst, and therefore the catalytic activity. This has now been addressed and the present work investigates the influence of cerium salt to urea synthesis ratio on the activity of a nanocrystalline ceria catalyst for naphthalene total oxidation.

2. Experimental

2.1. Catalyst preparation

A homogeneous precipitation method using the cerium salt ($(NH_4)_2Ce(NO_3)_6$, 99.9%, Aldrich,) and urea ($H_2N–CO–NH_2$, 100%, Aldrich) as precipitating agent was used to prepare ceria catalysts (denoted as CeO_2 (U)). To prepare a reference catalyst, a 1:3 ratio of $(NH_4)_2Ce(NO_3)_6$ and $H_2N–CO–NH_2$ were dissolved in 100 ml of deionised water. The resulting solution was stirred continuously and heated to 100 °C to form a brown gel-like solution, which was boiled and aged at 100 °C for 24 h. The solid obtained was filtered and dried at 120 °C. The resulting yellow solid was then calcined in static air at 500 °C for 6 h. In a series of further preparations the Ce salt/urea ratios of 2:1, 1:1, 1:2 and 1:4 were used to yield various CeO_2 (U) catalysts. The complete range of ceria catalysts prepared is detailed in Table 1.

2.2. Catalyst characterization

The surface areas of catalysts were determined by multi point N_2 adsorption at 77 K using the BET technique. Powder X-ray diffraction was used to identify the crystalline phases present in the catalysts. An Enraf Nonius PSD120 diffractometer with monochromatic Cu Kα source operated at 1.2 kW (40 keV and 30 mA) was used. The experimental patterns were calibrated against a silicon standard and phases were identified by matching against the JCPDS powder diffraction file. The crystallite size of diffracting domains was determined in accordance with the Scherrer method of X-ray line broadening. The reflections used were at 28.5° and 47.5° as these were the most intense reflections in the diffraction patterns.

A Renishaw system – 1000 dispersive laser Raman microscope was used for recording of Raman spectra. The excitation source used was an Ar ion laser (514.5 nm) operated at a power of 20 mW. The laser was focused on powdered samples placed on a microscope slide to produce a spot size of ca. 3 μm in diameter. A backscattering geometry with an angle of 180° between illuminating and collected radiation was used for data collection. Data were collected in the frequency range 200–1200 cm^{-1} with a resolution of ca. 0.4 cm^{-1}.

The particle size and morphology of powdered CeO_2 (U) catalysts were evaluated by scanning electron microscopy (SEM) using a Carl-Zeiss EVO 40 instrument. Images were obtained using a W filament and they were collected using back scattered and secondary electron modes. Images of samples were taken at high and low magnification to observe both the nature of particle morphology and the nature of the surface.

Temperature-programmed reduction studies were performed using a TPDRO 1100 Series Thermo Electron Corporation instrument with a TCD detector. In all experiments, 10% H_2 in Ar, at a constant flow rate of 20 ml min^{-1}, was used as reducing gas. A temperature range 30–600 °C was employed and a constant heating rate of 5 °C min^{-1} was used. 0.11 g of powdered catalyst was analyzed in each experiment.

2.3. Catalytic activity

Catalyst activity for naphthalene oxidation was determined using a fixed bed laboratory micro reactor. Catalysts were tested in powdered form using a 1/4 o.d. stainless steel reactor tube. The reaction feed consisted of 100 vppm naphthalene in air. A total flow rate of 50 ml min^{-1} was used and catalysts were packed to a constant volume to give a gas hourly space velocity of 45,000 h^{-1} for all studies. Analysis was performed by an on-line gas chromatograph with thermal conductivity and flame

Table 1
Effect of cerium salt to urea ratio on characteristics of CeO_2 (U) catalysts

Catalyst[a]	Surface area[b] ($m^2\,g^{-1}$)	Crystallite size[c] (nm)	Crystal phase[c]	FWHM [d] (cm^{-1})	TPR H_2 consumption[e] (μmol g^{-1})		r_{Np}[f] (mol m^{-2} min^{-1})
					LT peak	HT peak	
CeO_2, 2:1, 24 h, 500 °C/6 h	94	7.3	Cubic fluorite	28.6	10	176	12.2
CeO_2, 1:1, 24 h, 500 °C/6 h	94	7.2	Cubic fluorite	23.8	29	169	12.1
CeO_2, 1:2, 24 h, 500 °C/6 h	92	7.6	Cubic fluorite	19.6	15	189	2.7
CeO_2, 1:3, 24 h, 500 °C/6 h	125	7.5	Cubic fluorite	22.5	18	212	2.3
CeO_2, 1:4, 24 h, 500 °C/6 h	128	6.6	Cubic fluorite	28.0	4	235	10.2

[a] Catalyst, urea ratio, aging time, calcination temperature/calcination time.
[b] Calculated using the BET method.
[c] By XRD analysis.
[d] Full width at half maximum of the CeO_2 line in the Raman spectra.
[e] By TPR analysis, 110 mg of sample, 20 mL min^{-1} H_2, 5 °C min^{-1}.
[f] Naphthalene oxidation per unit surface area of ceria catalyst at 210 °C.

ionization detectors. Catalytic activity was measured over the temperature range 100–300 °C in incremental steps, and temperatures were measured by a thermocouple placed in the catalyst bed. Data were obtained at each temperature after a stabilization time. Three analyses were made at each temperature to ensure that steady state data were collected. The reaction temperature was increased and the same procedure followed to determine each data point. Reactions carried out in an empty reactor tube indicated that naphthalene conversion was negligible over the temperature range used in this study.

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows the properties of CeO_2 (U) catalysts prepared from five different ratios of cerium salt to urea. BET results show that these catalysts had surface areas in the range 92–128 $m^2\ g^{-1}$. Catalysts with cerium salt to urea ratios of 2:1, 1:1 and 1:2 had similar surface areas (92–94 $m^2\ g^{-1}$), whilst 1:3 and 1:4 ratios yielded catalysts with higher surface areas (125 and 128 $m^2\ g^{-1}$, respectively). XRD patterns of CeO_2 (U) prepared from varying cerium salt to urea ratios (Fig. 1) all showed diffraction peaks that were indicative of cubic fluorite ceria. There was no evidence for distortion of the ceria unit cell as the urea synthesis ratio was altered. A more detailed examination of the diffraction background and peak widths in the individual patterns suggested subtle differences in the crystalline nature of these catalysts. CeO_2 (U) catalysts derived from cerium salt to urea ratios of 2:1, 1:1 and 1:4 showed similarities in their crystalline nature and were slightly more crystalline than catalysts prepared from 1:2 and 1:3 ratios. The synthesis ratio did not significantly affect the ceria crystallite size as it was in the range 6.6–7.6 nm for all the catalysts, and hence they were nanocrystalline.

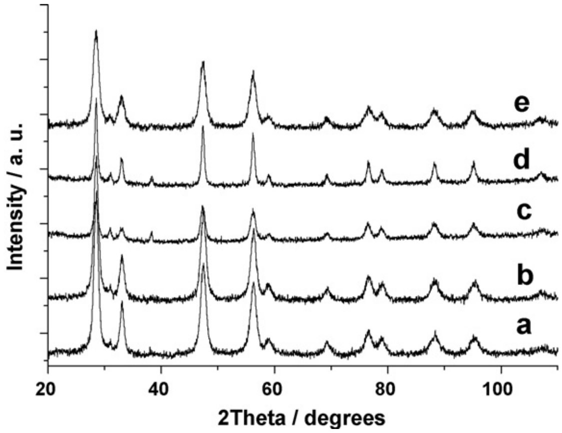

Fig. 1. Powder X-ray diffraction patterns of CeO_2 (U) catalysts prepared from different cerium salt to urea ratios (ageing time of 24 h, calcined at 500 °C for 6 h): (a) 2:1, (b) 1:1, (c) 1:2, (d) 1:3, (e) 1:4.

Raman spectra for the five catalysts with varying Ce salt/urea ratio (Fig. 2) were all similar, regardless of the cerium to urea ratio, showing a single intense Raman band centered at a Raman shift of 460 cm^{-1}. This band is characteristic of vibrations of CeO_2. It has been reported [31] that the values of the FWHM of the Raman band can be correlated with both the average crystalite size of ceria and the ceria defect concentration. An increase of the FWHM has been associated with a decrease of the crystallite size and/or a higher amount of oxygen vacancies in CeO_2. Since the crystallite size of the five ceria catalysts only varied slightly with the change in Ce salt/urea ratio, it can be assumed that an increase in FWHM corresponds to an increase in the concentration of oxygen defects. Ceria catalysts prepared from cerium salt/urea ratios of 2:1 and 1:4 showed considerably higher FWHM values (28.6 and 28 cm^{-1}, respectively) than the other three catalysts.

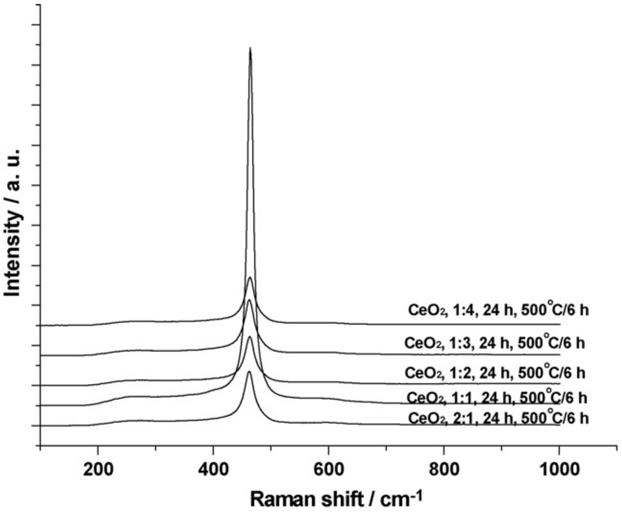

Fig. 2. Raman spectra of CeO_2 (U) catalysts prepared from different cerium salt to urea ratios.

The SEM images of catalysts prepared from varying Ce salt/urea ratios revealed a dependence of morphology and particle size of ceria on the Ce salt/urea ratio. There was considerable variation in the morphology of these catalysts with Ce salt/urea ratio. Catalysts with 2:1 and 1:1 ratios of Ce salt/urea showed some similarity in morphology, as they were composed of circular particles, all of which had fairly similar sizes for the same catalyst. However, particles in the catalyst with 2:1 ratio appeared to be smaller and showed a higher degree of agglomeration than those in the catalyst with 1:1 Ce salt/urea preparation. Particles in the latter (Fig. 3) existed as small circular particles with a very small degree of agglomeration. Catalysts with 1:2 and 1:3 Ce salt/urea ratios showed large irregular shaped particles, which appeared to provide centers of aggregation for smaller particles. The catalyst with Ce salt/urea ratio of 1:4 showed a rather unique morphology; comprised of relatively uniform-sized tiny particles, with some larger particles dispersed throughout the small particles. The small size of particles in this catalyst (1:4) relative to the other four catalysts agrees with the marginally lower crystallite size of the former as calculated by XRD analysis.

TPR profiles for the ceria catalysts (Fig. 4) demonstrated two main reduction bands between ambient temperature and 600 °C. A small low-temperature reduction peak centered at ca. 110 °C (denoted as LT peak) and a broader reduction band at

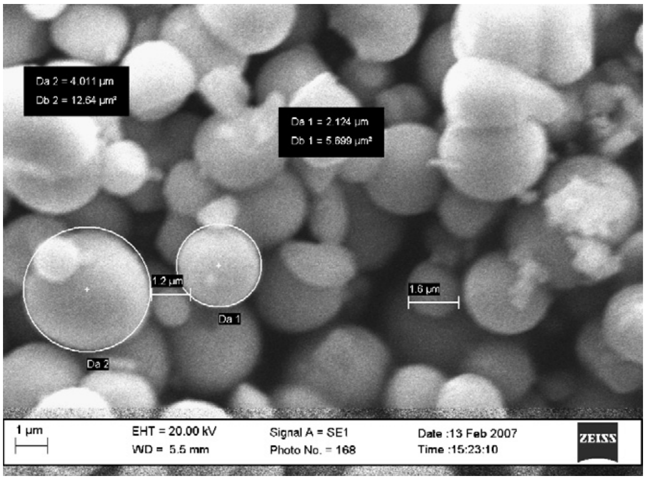

Fig. 3. Representative secondary electron SEM image of the ceria catalyst prepared using 1:1 cerium salt:urea.

higher temperature, from 300 to 600 °C (denoted as HT peak). The HT peak was comprised of two features centered at ca. 400 and 550 °C, respectively. The low reduction band is related to highly reducible surface ceria species, whereas the high-temperature reduction peaks can be attributed to surface reduction of capping oxygen species [31,32]. It must be noted that the reduction of the bulk of CeO_2 does not takes place over the range of temperature studied, since it only occurs above 750 °C [33]. It was observed (Table 1) that the total hydrogen consumption for these catalysts varied between 186 and 239 μmol g^{-1}. This variation was reflected in the values of hydrogen consumption both at low-temperature (4–29 μmol g^{-1}) and high-temperature (169–235 μmol g^{-1}) reduction features. The total hydrogen consumption increased as the Ce salt/urea ratio was decreased from 2:1 to 1:4. The variation in hydrogen consumption with cerium salt to urea ratio probably represents the formation of slightly different surface structures of ceria relating to the differences identified in morphology and particle size.

3.2. Naphthalene oxidation catalytic activity

Fig. 5 shows the effect of cerium salt to urea ratio on the activity of CeO_2 (U) catalyst for naphthalene oxidation. The activity of CeO_2 (U) prepared from a cerium salt to urea ratio of 1:4 was slightly higher than those from 1:1 and 2:1. The CeO_2, 1:4 catalyst equally showed an activity considerably higher than CeO_2, 1:2 and 1:3. Cerium salt/urea ratios of 1:4, 1:1 and 2:1 resulted in more efficient naphthalene oxidation catalysts than the 1:3 ratio employed for the synthesis of the reference catalyst [30]. CeO_2 (U) prepared from a 1:4 ratio had the highest surface area (128 m^2 g^{-1}), lowest crystallite size (6.6 nm) and the highest concentration of oxygen defects determined from the FWHM of Raman data, and we consider that these factors are important in determining the high activity of this catalyst. In previous work a strong relationship was established between the Raman FWHM and catalyst activity for a range of CeO_2 (U) catalysts prepared with varying calcination temperature, time and ageing time [30]. Weaker, but significant, correlations were also established between activity and surface area and crystallite size. In the present work no clear correlation between activity and Raman FWHM, surface area, crystallite size and surface reducibility can be established.

Considering the range of catalysts prepared there was a general increase of the naphthalene oxidation activity as the Raman FWHM increased (Fig. 6). Ceria catalysts with higher values of FWHM and hence higher oxygen defect concentrations (prepared from cerium salt/urea ratios of 2:1, 1:4 and 1:1) showed higher naphthalene oxidation activities than catalysts with lower FWHM (1:2 and 1:3). The relationship between Raman FWHM and activity in this work is not a strong relationship that has been observed previously [30], and suggests that the factors controlling activity of catalysts prepared using varied cerium to urea ratios are more complex.

Table 1 also shows the effect of cerium salt to urea ratio on the rate of naphthalene oxidation per unit surface area. Surface area normalized rates for the catalysts prepared with ratios of 2:1, 1:1 and 1:4 were significantly greater than the 1:2 and 1:3

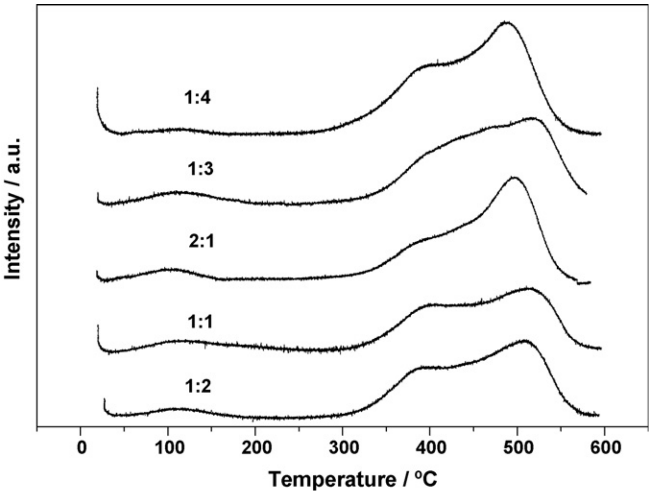

Fig. 4. Hydrogen temperature-programmed reduction profiles for CeO_2 (U) catalysts showing the influence of cerium salt to urea ratio.

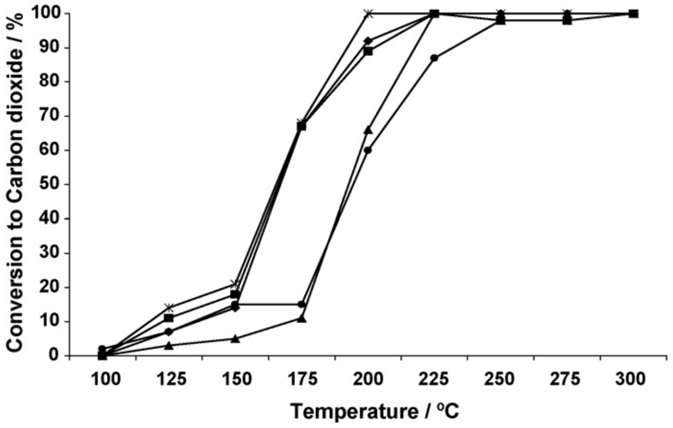

Fig. 5. Naphthalene total oxidation activity as a function of temperature for ceria catalysts prepared with varying cerium salt to urea ratio (catalysts aged for 24 h, and calcined at 500 °C for 6 h). Ce salt/urea ratio: (◆) 2:1, (■) 1:1, (▲) 1:2, (●) 1:3, (×) 1:4.

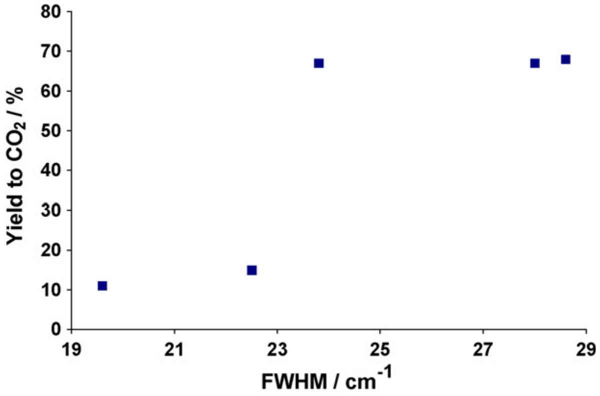

Fig. 6. Relationship between the FWHM of ceria Raman band and naphthalene total oxidation activity (yield to CO_2) at 175 °C.

catalysts. The 2:1 and 1:1 catalysts demonstrated similar normalized rates, which were marginally greater than the 1:4 catalyst. The normalized rates for 2:1 and 1:1 catalysts were approximately four times greater than the rate for the 1:2 catalyst. The surface areas of the 2:1, 1:1 and 1:2 catalysts were all similar (92–94 $m^2 g^{-1}$) and these data indicate that altering the synthesis ratio produced CeO_2 with subtly different surfaces resulting in differences of activity. The same conclusion can also be made by considering the normalized activity of 1:3 and 1:4 catalysts. It is also noteworthy that the relationship between surface area normalized rates and Raman band FWHM are similar to that presented in Fig. 6. This observation suggests that changing the cerium to urea ratio not only resulted in different surface structures that influence activity, but the concentration of oxygen defects is also an important factor in determining catalyst activity.

An indication of the different surface structures of the catalysts can be derived from consideration of the surface reducibility, from TPR data, and the differences of morphology, from secondary electron SEM images. The 2:1 and 1:1 catalysts, which were amongst the most active and showed the same surface area normalized rate, have the same morphology, which was distinct from the other catalysts. The 1:4 catalyst demonstrated a comparable naphthalene total oxidation rate similar to the 2:1 and 1:1 catalysts, whilst the surface area normalized rate was slightly lower. In addition to having a very different morphology to the 2:1 and 1:1 catalysts, the 1:4 catalyst also showed a smaller lower-temperature and a greater high-temperature peak in the TPR profile. Furthermore, the 1:4 catalyst showed a reduction feature that was shifted to a lower temperature and indicates that the surface oxygen species were more labile. The differences in surface reducibility are most likely influenced by the catalyst morphology and not the crystallite size as this did not alter significantly. Therefore, it can be concluded that changing the cerium to urea ratio neither strongly influences the bulk structure of the ceria, nor greatly influence the surface area and crystallite size. However, it did influences the morphology, surface reducibility and oxygen defect concentration of the catalysts. These latter factors were more important for the catalyst activity. There is no simple relationship between the activity and the features of the catalysts characterized and it is a combination of the factors outlined above, which contribute to varying degrees that ultimately determine catalyst activity. This work continues, and high-resolution TEM and XPS studies are planned to elucidate more fully the catalyst structure and surface properties.

The importance of using an appropriate amount of urea during the preparation method must be highlighted. It is proposed that morphology, reducibility and defect concentration determine the catalytic activity. Thus, a low urea content (2:1) seems to present a greater defect concentration that leads to high activity. Further increase of the urea ratio (1:2 and 1:3) leads to a change of the morphology as well as a decrease in the defect concentration, decreasing the catalytic activity. Finally the catalyst with the highest urea content (1:4) presents the highest surface area and the smallest particle size that in combination with the high defect concentration and morphology can increase the naphthalene conversion.

From a combination of the naphthalene oxidation activity results over CeO_2 (U) reported in recent work [30] and the catalytic activity data reported in this work, it can be noted that a range of preparation variables influence catalyst activity for naphthalene total oxidation. In this study the most active catalyst was prepared using: a cerium salt to urea ratio of 1:4, aging time of 12 h, calcination temperature of 500 °C and a calcination time of 6 h. The use of these preparation conditions yielded a CeO_2 (U) catalyst with a relatively high surface area (126 $m^2 g^{-1}$) and small crystallite size (5.4 nm). Fig. 7 shows the effect of gas hourly space velocity on the activity for naphthalene total oxidation. As expected the conversion decreased as GHSV was increased. However, even at a relatively low temperature of 175 °C it was possible to achieve very high naphthalene conversion by operating at a GHSV of 25000 h^{-1}. The activity data demonstrate that it is possible to produce very active metal oxide catalysts, based on ceria, for the total oxidation of naphthalene, which is an excellent model for the toxic class of VOCs known as polycyclic aromatic hydrocarbons.

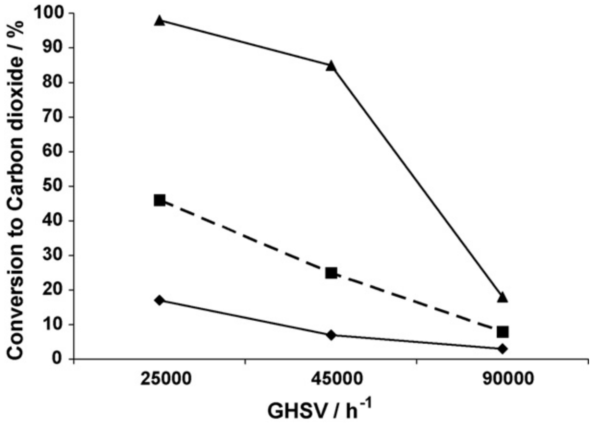

Fig. 7. Plot showing the effect of GHSV on the naphthalene total oxidation activity of CeO_2 (U) prepared using optimum preparation conditions. (◆) 125 °C, (■) 150 °C, (▲) 175 °C.

4. Conclusions

It has been shown that the activity of a CeO_2 catalyst prepared by homogeneous precipitation with urea for naphthalene total oxidation can be influenced by varying the ratio of starting materials (Cerium salt to urea ratio). A variation of this ratio resulted in slight differences of surface area and crystallite size of the ceria catalyst. However, a mark variation in oxygen defect concentration (FWHM of the characteristic Raman band) of the CeO_2 (U) and morphology was observed upon varying the cerium salt to urea ratio. The oxygen defect concentration influences the catalyst activity. Whilst the different morphologies are thought to influence the surface structure of the ceria, and this was evident from subtle variations of the surface reduction behavior. The differences of oxygen vacancy concentration coupled with the change of morphology with cerium salt to urea ratio have been suggested to be the main factors accounting for the variations of naphthalene oxidation activity.

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