



Total oxidation of naphthalene with high selectivity using a ceria catalyst prepared by a combustion method employing ethylene glycol

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ABSTRACT

During the catalytic combustion of naphthalene, compounds other than CO₂ are often obtained. These products, as polymerized polycyclic aromatic hydrocarbons, oxygenated aromatic compounds and benzene derivate compounds, are usually more toxic than naphthalene. At the present work it is shown a nanocrystalline cerium oxide prepared by a combustion method employing a proper ethylene glycol concentration that exhibits very high activity in the decomposition of naphthalene in the presence of air and, most importantly, a selectivity value towards CO₂ of 100% for any range of conversions and/or temperatures used. In addition, it has been demonstrated that the amount of ethylene glycol employed in the synthesis of the catalyst is determinant to achieve the optimal catalytic performance. The catalytic results have been explained in terms of the amount of cerium oxide defects.

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1. Introduction

In recent times new methods for the abatement of pollutants have been developed, and these have been required due to the increasing enforcement of environmental regulations and to an increase of ecological awareness. Amongst these methods we can highlight biodegradation [1], high-energy electron beam [2], ozonization [3], adsorption [4], absorption [5], thermal incineration [6] and catalytic oxidation [7–10] as potential pollution control methods. In particular, the release of polycyclic aromatic hydrocarbons (PAHs) has started to cause considerable concern. The main source of these atmospheric pollutants is the combustion of fossil and non fossil fuels, such as diesel, gasoline, biomass, coal and wood [11–14]. The emission of PAHs from diesel vehicles is becoming more and more important due to the progressive worldwide substitution of gasoline fuelled vehicles by those that use diesel.

The catalytic oxidation of PAHs has been demonstrated to be one of the most cost-effective amongst all PAH abatement techniques, due to the lower combustion temperatures required and the higher selectivity towards CO₂, compared to most of the other methods. Unfortunately, the destruction of reactants via oxidation can still generate by-products as secondary pollutants, which in most of the

cases could be more toxic than the parent products. Hence achieving high selectivity to completely oxidised products is an important aim.

Naphthalene is the simplest, most volatile and least toxic of the PAHs [11,15]. In fact naphthalene has been used in several research laboratories [8,10,16–20] as a model to develop catalysts with potential to effectively destroy PAHs. To date the majority of catalysts studied for PAH abatement are precious metal based, and some of the most active are Pt/Al₂O₃ [8,16,17] and Pt/V/Al₂O₃ [10]. In both cases, in spite of the effectiveness of Pt/Al₂O₃ as a naphthalene abatement catalyst, it has been found to produce intermediates other than CO₂ and H₂O during the naphthalene oxidation process [21]. Naphthalene derivatives, polymerized polycyclic aromatic hydrocarbons and polymerized-oxygenated polycyclic aromatic compounds were found in the reaction products [8], not only in the gas phase but also on the catalyst surface.

On the other hand, it has recently been demonstrated that nanocrystalline CeO₂ catalysts, prepared by homogeneous precipitation with urea, were significantly more effective for naphthalene total oxidation when compared to the activity of a wide range of metal oxide catalysts [22,23]. Furthermore, comparison with a supported Pt catalyst also showed that the urea precipitated ceria catalyst was more active. However, at lower reaction temperatures naphthalene conversion was high, whilst selectivity to CO₂ was below 100%, and a range of toxic by-products could be detected in the gas phase, i.e. naphthol, phenanthrene and phthalate

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derivatives [23]. Even though at higher reaction temperatures complete selectivity to CO₂ was achieved, there still remains scope to identify PAH oxidation catalysts, which are more selective to CO₂ across a wider range of operating conditions.

Nanopowders of CeO₂ can be prepared by a range of different procedures, including mechanochemical, hydrothermal, sol–gel, precipitation and combustion methods. Self-sustaining combustion synthesis is a simple method that can produce homogeneous, pure and relatively high surface area ceria catalysts [24,25]. In this preparation procedure an oxidizing agent and a fuel combines, releasing heat due to the exothermicity of the reaction, leading to the formation of an oxide phase, in this case CeO₂.

Against this background, here we show that CeO₂ catalysts, prepared by a simple combustion method with ethylene glycol, present appreciably high catalytic activity and an extremely high selectivity to CO₂ and H₂O when used for the oxidation of a model PAH. It is also shown that the physico-chemical and catalytic properties of the CeO₂ prepared depend on the amount of ethylene glycol employed. Thus, total selective catalysts with relatively high activity can be synthesized when appropriate conditions are employed.

2. Experimental

2.1. Catalyst preparation

The catalysts were synthesized through a combustion method employing ethylene glycol (EG) as a fuel for the reaction. The source of cerium (NH₄)₂Ce(NO₃)₆ was supplied by Sigma–Aldrich as well as the EG (HOCH₂CH₂OH, Sigma–Aldrich). Different molar ratios were obtained: $k = 50; 75; 100; 125$ and 150 , where $k = 100 \times$ (moles of EG/moles of Ce). Thus, adequate quantities of both compounds to produce 3 g of CeO₂ were dissolved in 50 ml of distilled water. This aqueous solution was heated on a hot plate stirrer at 400 °C. The mixture initially lost water and transformed into a gel and eventually a solid was obtained following a violent reaction. The solids obtained were heat-treated in flowing air for 4 h at 400 °C to produce the catalyst. This series of catalysts has been called Ce-EG and the particular catalysts Ce-k.

2.2. Catalytic tests

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. quartz tube as reactor. The feed-stream consisted, in all cases, of 450 ppmv naphthalene in air. Under the standard conditions a total flow rate of 50 ml min⁻¹ and a gas hourly space velocity (GHSV) of 45 000 h⁻¹ was employed.

Analysis of reactants and reaction products were performed by an on-line gas chromatograph with thermal conductivity and flame ionization detectors. Catalytic activity was measured over the temperature range 100–400 °C in incremental steps, and temperatures were measured by a thermocouple placed in the catalyst bed connected to a PID controller. Data were obtained at each temperature after a stabilization time. Three analyses were made at each temper-

ature to ensure that steady state data were collected. The reaction temperature was increased and the same procedure followed to determine each data point.

2.3. Catalyst characterization

The surface areas of catalysts were determined by multi point N₂ adsorption at 77 K in a Micromeritics ASAP 2000 V2.04 phys/chemisorption unit, using the BET technique.

Powder X-ray diffraction was used to identify the crystalline phases present in the catalysts. A Bruker D8 Advance diffractometer with monochromatic Cu K α source operated at 40 kV and 40 mA) was used. The experimental patterns were obtained analysing from 3° to 80° with an angle increment of 0.05° and an accumulation time of 3 s. Finally, the phases present were identified by matching experimental patterns to the JCPDS powder diffraction file.

A confocal micro-Raman spectrometer (Horiba Jobin Yvon HR800 UV) was used for recording of Raman spectra. The green laser (532 nm), operated at a power of 40 mW, was focused on powdered samples placed on a microscope slide to produce a spot size of ca. 8 μ m in diameter. The detector used was an air-refrigerated charge-coupled device (CCD).

The particle size and morphology of powdered 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 Micromeritics Autochem II instrument with a TCD detector. In all experiments, 10% H₂ in Ar, at a constant flow rate of 50 ml min⁻¹, was used as reducing gas. A temperature range of 30–1000 °C was employed and a constant heating rate of 10 °C min⁻¹ was used to analyse 0.30 g of powdered catalyst in each experiment.

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. 500 ppm naphthalene in synthetic air with a total flow of 20 ml min⁻¹ was maintained by mass-flow controllers. Prior to the *in-situ* adsorption or reaction measurements by DRIFTS at 250 °C, the samples were activated at 350 °C for 30 min in a synthetic air-flow and then cooled to 250 °C. 64 scans were collected with a spectral resolution of 4 cm⁻¹. The spectra shown were obtained after subtraction of the features of the catalyst, recorded at 250 °C in He.

3. Results

3.1. Characterization results

Some characteristics of the CeO₂ catalysts synthesized by the combustion method employing ethylene glycol (EG) are summa-

Table 1
Physico-chemical and catalytic characteristics of cerium oxide catalysts prepared by a combustion method using ethylene glycol (EG) as a fuel.

Catalyst	EG/Ce molar ratio	TPR bands (°C)	S _{BET} (m ² g ⁻¹)	CeO ₂ crystallite size ^b (nm)	FWHM _{Raman} (cm ⁻¹)
Ce-50	0.50	377, 480, 850	34	17	29
Ce-75	0.75	372, 472, 858	40	16	35
Ce-100	1.00	372, 481, 845	49	14	32
Ce-125	1.25	372, 483, 850	64	14	31
Ce-150	1.50	376, 475, 855	57	14	30
CeO ₂ (U) ^a	–	–	171	5	37
CeO ₂ (P) ^a	–	–	87	5	33

^a According to [23]. CeO₂(U) prepared using urea. CeO₂(P) prepared by precipitation with carbonates.

^b By XRD using the Sherrer's equation.

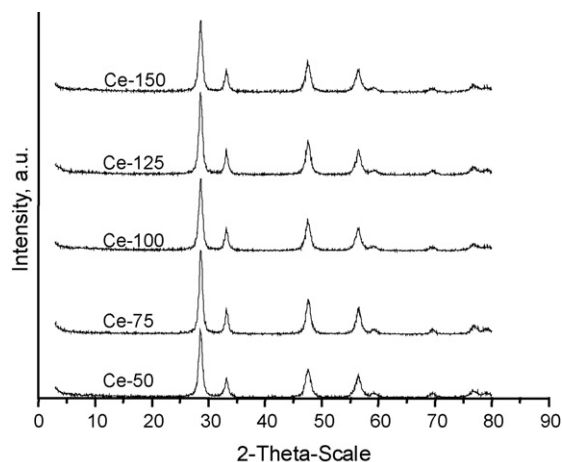
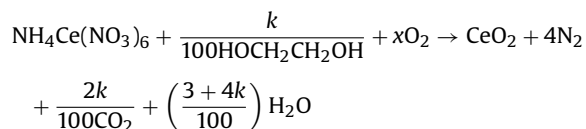


Fig. 1. XRD patterns of CeO₂ catalysts prepared by a combustion method employing ethylene glycol as a fuel (Ce-EG samples).

ized in Table 1. For a comparative purpose the characteristics of two CeO₂ prepared by two different methods [23], CeO₂(U) (homogeneous precipitation with urea) and CeO₂(P) (precipitation with carbonate) have also been included. The surface area measurements, treated according to the BET method, indicate that the use of ethylene glycol leads to surface areas between 30 and 64 m² g⁻¹. The higher the EG content, the higher is the surface area of the catalysts. Above an EG/Ce ratio of 1.25 no further increase of surface area was observed.

For the preparation route with EG the expected reaction was:



The nature of the Ce-material obtained (CeO₂) was confirmed by XRD (Fig. 1). According to XRD results the same crystalline phase was observed in all cases, cubic fluorite CeO₂, although differences in the crystallite size (estimated using the Scherrer equation) have been observed. The relationship showed that the higher the EG concentration, the lower the crystallite size of ceria (Table 1). Above an EG/Ce ratio of 1.00 no further variation has been observed.

Raman spectra were also recorded for all catalysts (Fig. 2). All CeO₂ catalysts showed one high intensity Raman band centred at a Raman shift of 460 cm⁻¹ typical of CeO₂ vibrations (the triply

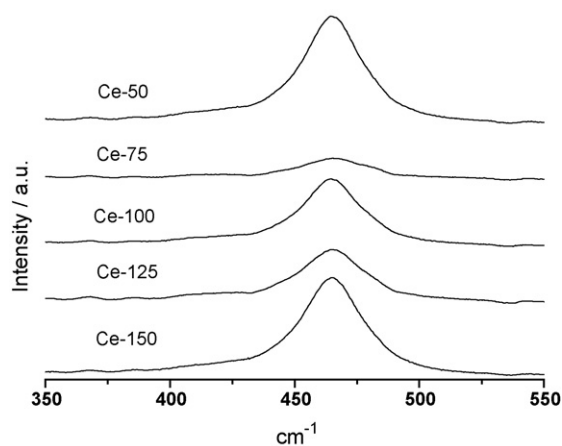


Fig. 2. Raman spectra of CeO₂ catalysts prepared by a combustion method employing ethylene glycol as a fuel (Ce-EG samples).

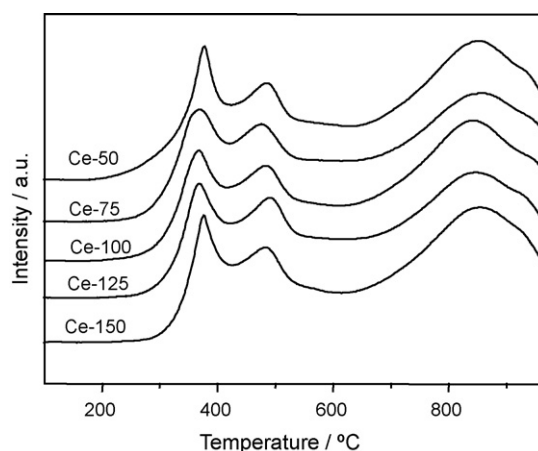


Fig. 3. TPR profiles of CeO₂ catalysts prepared by a combustion method employing ethylene glycol as a fuel (Ce-EG samples).

degenerate TO mode) [26]. No clear trend can be observed between the intensity of the Raman band and the EG/Ce ratio. In Table 1 the values for the full width at half maximum (FWHM) of the Raman band at 460 cm⁻¹ are presented. It can be observed that the FWHM is, in all cases, in the 29–35 cm⁻¹ range, with Ce-75 the highest value (35 cm⁻¹).

TPR experiments from room temperature to 1000 °C were carried out on the ceria catalysts prepared by the combustion method (Fig. 3). Three main reduction bands were observed in all catalysts, at ca. 370, 480 and 850 °C. The bands centered at ca. 370 and 480 °C, respectively, can be assigned to surface reduction of capping oxygen species [27,28], meanwhile the band at 850 °C is ascribed to the reduction of the bulk of CeO₂ [27,29,30]. Minor differences have been observed between these catalysts, when the H₂ consumption and the position of the reduction bands are considered. In addition, TPR profiles for the urea and carbonate precipitated catalysts were similar to those previously reported [30].

Fig. 4 shows the SEM images for catalysts prepared by the combustion method. The morphology of the particles is significantly different depending on the amount of ethylene glycol employed during the synthesis. In the case of the sample with the lowest amount of EG (Ce-50) two different types of morphology could be appreciated: many agglomerated units of tiny particles with a diameter of approximately 200–400 nm and a lower number of intergrown particles with a considerably smaller size. Ce-75 sample mainly presents independent and relatively regular particles of 70–120 nm. Smaller grains could be appreciated with “cloud-like” shapes. In the case of Ce-100 intergrown particles of 50–80 nm are observed. Finally, the sample prepared with the highest amount of EG, Ce-150, exhibits the smallest particles, 20–30 nm. Some other agglomerates of 100–200 nm were also detected, although they were in the minority.

3.2. Catalytic performance

Fig. 5 shows the evolution of the Np conversion in the oxidative decomposition of naphthalene with the reaction temperature, for cerium oxide based catalysts prepared by the combustion method using various amounts of ethylene glycol. It can be observed that the amount of EG used in the preparation method has an influence on the catalytic performance. Different trends have been observed when comparison of activity is made at high and low Np conversion. At low reaction temperatures (up to 200 °C) the Np conversion is the highest in those catalysts prepared with the highest EG concentrations. At reaction temperatures over 200 °C an intermediate EG/Ce ratio seems to be the most appropriate. Thus, the catalyst

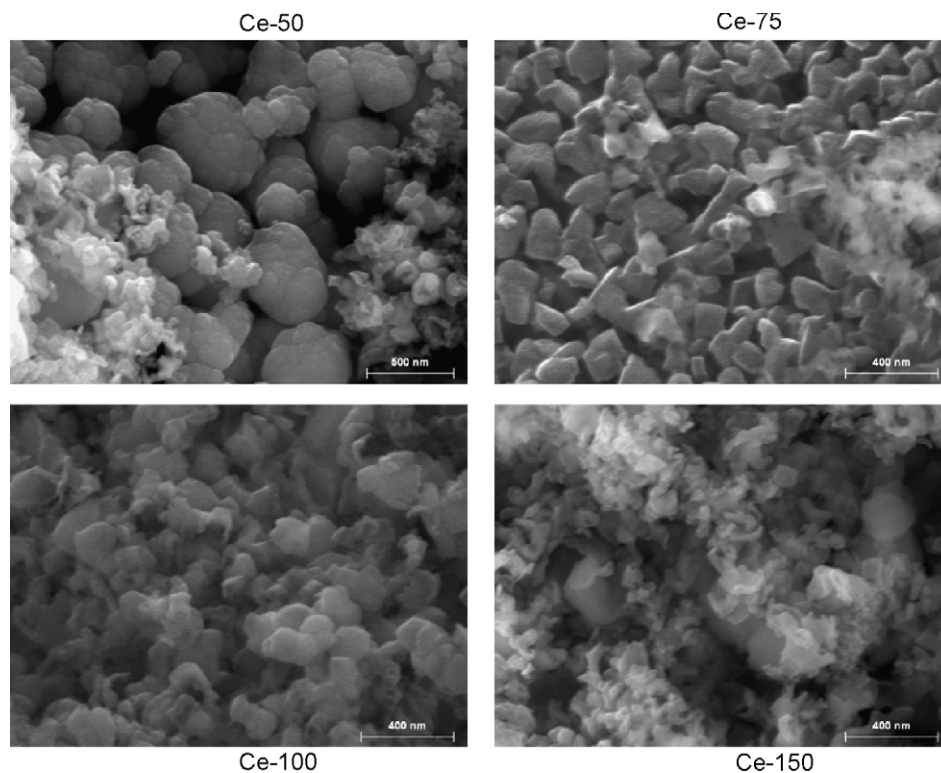


Fig. 4. SEM images of CeO₂ catalysts prepared by a combustion method employing ethylene glycol as a fuel (Ce-EG samples).

with an EG/cerium mol. ratio of 0.75 showed the highest activity of all catalysts tested, achieving almost a total conversion at 250 °C.

More important than the Np conversion is the yield to CO₂ since many toxic by-products can be generated during the Np combustion processes. In this way Fig. 6 shows the evolution of the yield to CO₂ obtained with the reaction temperature. Similarly to the Np conversion (Fig. 5), the highest activity expressed as yield to CO₂ at reaction temperatures of 200 °C and below correspond to the catalysts with high EG concentrations (Fig. 6B). Over that temperature Ce-75 presented the highest yield. According to Table 2, it can be clearly observed that the selectivity towards CO₂ was very high in all catalysts tested achieving at least 90% when the Np conversion reaches 50%. It must be remarked that in the case of Ce-75 catalyst it presented a selectivity to carbon dioxide of ca. 100% in all the exper-

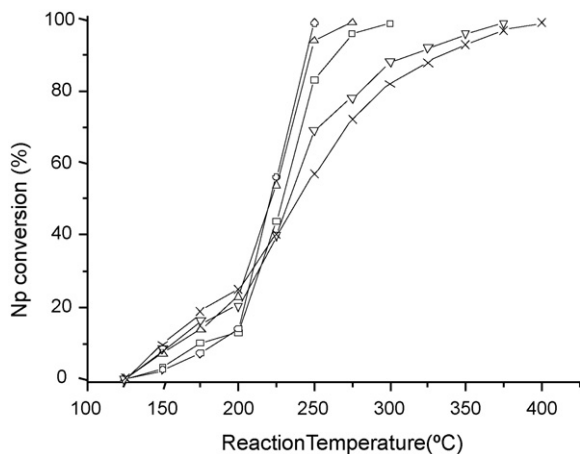


Fig. 5. Variation of the naphthalene conversion with the reaction temperature. Catalysts: (□) Ce-50, (○) Ce-75, (△) Ce-100, (▽) Ce-125, (x) Ce-150. Reaction conditions in text, GHSV = 45000 h⁻¹.

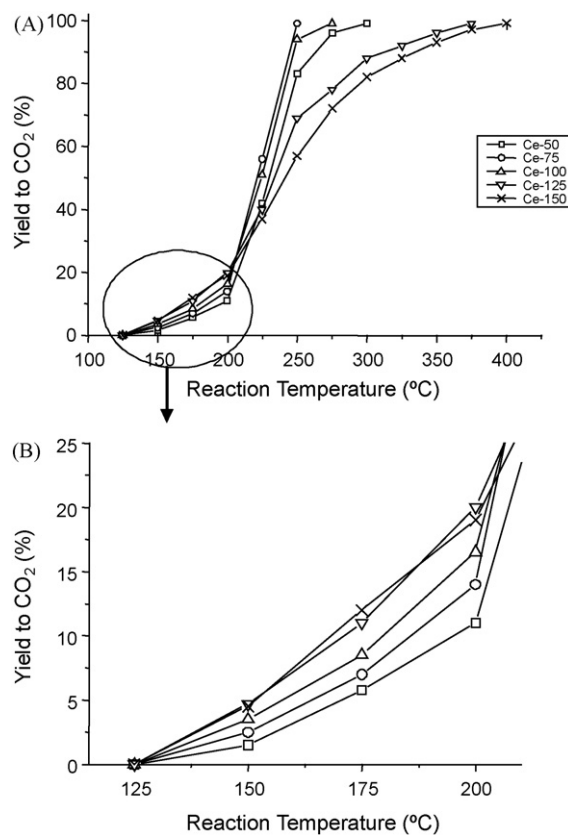


Fig. 6. Variation of the yield to CO₂ during the naphthalene oxidation with the reaction temperature. (A) shows the data in the 100–425 °C temperature range. (B) shows the same data from 100 to 200 °C. Catalysts: (□) Ce-50, (○) Ce-75, (△) Ce-100, (▽) Ce-125, (x) Ce-150. Reaction conditions in text, GHSV = 45000 h⁻¹.

Table 2

Selectivity values for Ce-EG catalysts at the same conversion. S_{20} , selectivity at 20% naphthalene conversion; S_{50} , selectivity at 50% naphthalene conversion.

Catalyst	Selectivity to CO ₂	
	S_{20} (%)	S_{50} (%)
Ce-50	87	97
Ce-75	>98	>98
Ce-100	90	98
Ce-125	79	96
Ce-150	80	96

iments undertaken. This is in contrast to many other catalysts used for Np oxidation (see below), as often relatively low selectivities to CO₂ are observed when the catalyst shows initial activity, and high CO₂ selectivity is obtained only at higher reaction temperatures.

It must be indicated that stability tests have been conducted over some of these catalysts (Ce-50, Ce-75 and Ce-150). After 9 h on line no deactivation at a reaction temperature of 225 °C was appreciated. To determine the long-term stability further experiments are required.

A comparative study of these catalysts with other cerium oxide catalysts, prepared by different procedures, was carried out. Fig. 7 compares both the activity (7A) and the selectivity towards CO₂ (7B) of one of the catalysts synthesized employing EG (Ce-75) with

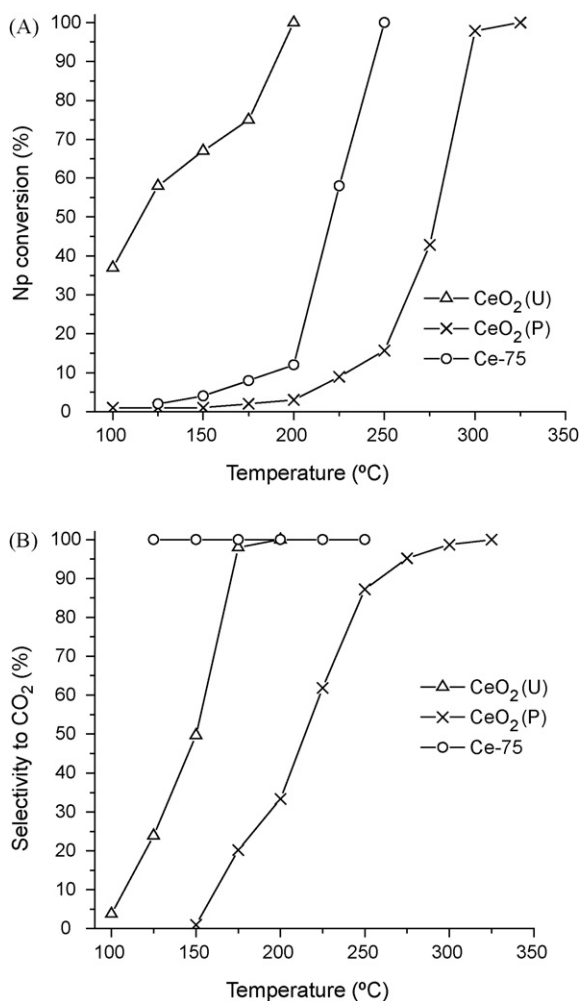


Fig. 7. Evolution of the naphthalene conversion (7A) and the selectivity to CO₂ (7B) with the reaction temperature for CeO₂ catalysts prepared by different methods. Catalysts: (○) Ce-75, (Δ) CeO₂(U), (x) CeO₂(P). Reaction conditions in text, GHSV = 45000 h⁻¹.

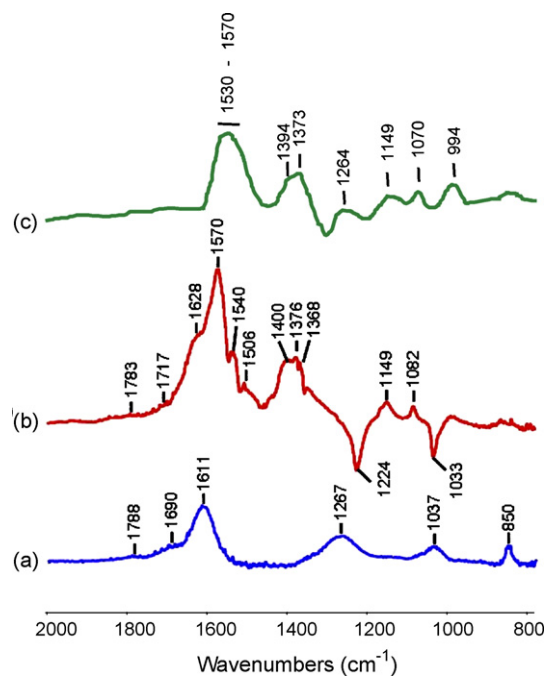


Fig. 8. In situ-DRIFT spectra of (a) CeO₂(P), (b) CeO₂(U) and (c) Ce-75 feeding 100 ppm naphthalene in air. Note: experiments carried out at 250 °C after 90 min.

other cerium oxide catalysts. The catalysts used for comparison are (i) carbonate precipitated ceria, CeO₂(P), and (ii) a highly active catalyst precipitated using urea, CeO₂(U), both previously reported in the literature [22,23]. Ceria with the highest surface area, CeO₂(U), achieves much higher conversion than the catalysts prepared in the present study. For example, CeO₂(U) presents almost total conversion at 200 °C, meanwhile the sample with EG achieves equivalent activity at 250 °C. This difference is most likely due to the higher surface area and lower crystallite size of those prepared with urea (ca. 170 m²/g with urea versus ca. 40 m²/g with EG). Fig. 7B shows the selectivity to CO₂ of these ceria samples. It can be observed that whilst Ce-75 is totally selective to CO₂ in the full range of conversions, CeO₂(U) and CeO₂(P) catalysts always lead to others sub-products than CO₂, even at high naphthalene conversions.

3.3. In situ-DRIFTS catalytic study

In order to develop some understanding of the differences in catalytic behaviour, *in-situ* DRIFTS experiments were also conducted for naphthalene oxidation (450 ppm naphthalene in synthetic air) at 250 °C over CeO₂(P), CeO₂(U) and Ce-75 (Fig. 8). These spectra are shown in the 2000–800 cm⁻¹ range, which corresponds to the CO and CC stretching regions. The spectra were very different depending on the catalyst considered, and the assignments of the peaks observed are shown in Table 3. In summary, CeO₂(P) contains signals related to aromatic ring vibration of a species adsorbed parallel to the catalyst surface (1611 cm⁻¹, high intensity), partially oxidised adsorbed species (1690 and 1788 cm⁻¹, low intensity) and to bidentate carbonates (850, 1037 and 1267 cm⁻¹, medium intensity).

The spectrum of CeO₂(U) shows peaks related to a loss of bidentate carbonate species during reaction (1037 and 1224 cm⁻¹, negative peaks), to a surface bidentate formate species formed during the partial oxidation of naphthalene (1368–1400, 1540 and 1570 cm⁻¹, high intensity), aromatic ring vibrations of a species adsorbed parallel to the catalyst surface (1628 cm⁻¹, high intensity) and to adsorbed partial oxidation species (998, 1082, 1149, 1717 and 1783 cm⁻¹) were observed.

Table 3
Assignment of in situ-DRIFTS data of cerium oxide prepared by different procedures^a.

Catalyst	Bands/peaks	Intensity	Assignment
Ce-75 ^b	994, 1070, 1149	Medium	Phthalates
	1264	Medium	Bidentate carbonates
	1370–1395	High	Surface bidentate formate formed in reaction
	1530–1570	High	Surface bidentate formate formed in reaction
	1690	Very low	Naphthoquinones
CeO ₂ (U)	998, 1082, 1149	Medium	Phthalates
	1037 (negative)	Medium	Loss of carbonates during reaction
	1224 (negative)	Medium	Loss of carbonates during reaction
	1368–1400	High	Surface bidentate formate formed in reaction
	1540, 1570	Very high	Surface bidentate formate formed in reaction
	1628	High	Aromatic ring vibrations (surface species)
	1717	Very low	Naphthoquinones
1783	Very low	Phthalic anhydride	
CeO ₂ (P)	850, 1037, 1267	Medium	Bidentate carbonates
	1611	High	Aromatic ring vibrations (surface species)
	1690	Very low	Naphthoquinones
	1788	Very low	Phthalic anhydride

^a Assignments of bands according to Refs. [32–38], mainly from Ref. [32].

^b In-situ DRIFTS of the other catalysts of the Ce-EG series present very similar spectra.

Finally, the catalyst prepared by the combustion method shows peaks related to a surface bidentate formate species formed during the partial oxidation of naphthalene (1373, 1394 and 1530–1570 cm⁻¹, high intensity), and adsorbed partial oxidation species with low and medium intensity (994, 1070, 1149, 1690 cm⁻¹).

Thus, the main differences between the catalyst prepared by combustion with the other two are: (i) the absence of the band at 1600–1630 cm⁻¹ indicative of the presence of aromatic rings on the surface and (ii) the predominant presence of a high degree of naphthalene decomposition products (bidentate formates) versus a low degree of naphthalene decomposition products (naphthoate, naphthoquinones, phthalic anhydride and phthalates)

4. Discussion

Although the main, and desired, reaction product detected for naphthalene catalytic oxidation is CO₂, a number of other reaction products have often been identified and reported, and these depend on the catalyst and/or the reaction temperature used. Detected products reported in the literature [8,23] include naphthol, phenanthrene, naphthalene dione, dimethyl phthalate, benzene, trimethyl benzenes, benzaldehyde, toluene, xylenes, acetophenone, benzoic acid, benzyl alcohol and polyaromatic compounds. In all cases, the concentration of these by-products was very low and the presence of these by-products was demonstrated by capturing these compounds in a dichloromethane cold trap at the exit of the reaction system and analyzing them by GC-MS.

In this work, it has been shown that the use of ethylene glycol as a fuel to prepare nanocrystalline cerium oxide by a combustion method leads to active and extremely selective catalysts for the total oxidation of naphthalene. The most outstanding feature of the catalysts prepared by combustion using EG is the high selectivity to CO₂. During the catalytic oxidation of naphthalene other partially oxidised compounds, in addition to CO₂, are often obtained. Many of these products, such as benzene, toluene, xylene and polyaromatic related compounds, are potentially more toxic than naphthalene, and hence can be detrimental. By using Ce-EG

catalysts it can be ensured that a high selectivity to CO₂ can be achieved, especially in the case of the Ce-75 catalyst, as 100% selectivity was observed regardless of the reaction temperature tested. The other ceria catalysts prepared by different methods (CeO₂(U), CeO₂(P)) only achieved 100% selectivity at full naphthalene conversion (Fig. 7B).

In terms of activity, it is worth to point out that Ce-EG catalysts are not very active catalysts. Indeed, these catalysts show a catalytic activity remarkably lower than CeO₂(U) catalyst, according to its much higher specific surface area and lower crystallite size. Regarding to CeO₂(P) catalyst, it has been previously reported [32] that the presence of carbonates contaminating the catalyst surface is negatively affecting its catalytic activity, so that Ce-EG catalysts exert higher activity although these catalysts present lower specific surface area and higher crystallite size.

However, Ce-EG catalysts show an outstanding selectivity to CO₂ in the full range of conversions. A tentative explanation for this high selectivity achieved by the catalysts prepared by the combustion method can be proposed. The value of the FWHM obtained from Raman spectroscopy has been widely reported [27,31] to be correlated with both the average crystallite size of ceria and the defect concentration in the ceria structure. Correspondingly a high FWHM is associated with a low crystallite size and/or a high amount of oxygen vacancies in the CeO₂ structure. The catalysts prepared using EG present a CeO₂ crystallite size of ca. 15 nm and a FWHM of ca. 35 cm⁻¹. Both CeO₂(U) and CeO₂(P) catalysts presented a CeO₂ crystallite size of ca. 5 nm with a FWHM of ca. 37, and 33 cm⁻¹ respectively. Accordingly, Ce-EG samples are likely to present a much higher number of oxygen vacancies than the others prepared using the different methods, since the crystallite size of these catalysts is remarkably higher than those of CeO₂(P) and CeO₂(U) catalysts. It must be noted that due to the different reaction temperature that these catalysts need to activate the substrate, it is very likely that the reaction temperature (and not only the Np conversion) also has an influence on the selectivity to CO₂.

For the Ce-EG samples, although it is not possible to establish a correlation between the FWHM and the selectivity values, it can be observed that the higher the FWHM, the higher the selectivity values at the same conversion (see Table 2), for those groups of Ce-EG catalysts with similar crystallite size. Thus, Ce-75 is more selective than Ce-50; and Ce-100 is more selective than Ce-125 and Ce-150, respectively. It is worth to point out that the Ce-EG series selectivity always was in the range of 95–100% and, in the case of Ce-75, the selectivity was 100%.

Taking into account the characterization and catalytic results, we relate the presence of a high concentration of vacancies to the deep oxidation of naphthalene (i.e. very high selectivity to CO₂) rather than to the overall activity. The oxygen vacancies are likely to be involved in the surface oxidation of the reaction intermediates from naphthalene to CO₂, but they are not the unique feature of the catalyst for the activation of the naphthalene molecules. Accordingly, in situ-DRIFTS data have shown that a high degree of naphthalene decomposition products are predominant from those catalysts with a higher concentration of oxygen vacancies (see Table 1). The overall activity will also be influenced by the specific surface area, the reducibility, the crystallite size and the morphology [30]. In fact, at low conversions of naphthalene the most active catalysts have been those with the highest surface areas and smallest particle size (those with the highest EG/Ce ratio, Ce-125 and Ce-150), where the number of active sites is higher and the naphthalene activation to form low degree of naphthalene oxidation surface products, i.e. naphthoates and phthalates, seems to be favoured. However, the catalytic activity increases more drastically in those catalysts with the lowest EG/Ce ratio (Ce-50, Ce-75 and Ce-100), especially in the case of Ce-75, the catalyst with the highest Raman FWHM (35 cm⁻¹) and

possibly the one with the highest concentration of oxygen vacancies, where it is favoured the total oxidation of naphthalene.

It is not necessarily straightforward to explain the higher selectivity to CO₂ achieved by catalysts prepared by the combustion method compared to other CeO₂ catalysts. Maybe the highly exothermic ethylene glycol oxidation reaction that takes place during the preparation procedure of these catalysts can favour the appearance of oxygen vacancies, which seem to avoid the formation of condensed polyaromatic compounds and to ease the total oxidation of surface reaction products (see DRIFTS data). Although all the catalysts of the Ce-EG series are rather active the results obtained clearly vary depending on the EG/Ce ratio. During the combustion method, depending on the fuel (EG) to oxidiser (Ce-salt) ratio, the contact between the fuel and the salt or the flame temperature are modified. This leads to different amounts of oxygen vacancies, which can influence the physico-chemical and the catalytic characteristics of the samples synthesized.

5. Conclusions

Nanocrystalline cerium oxide catalysts have been prepared by a simple combustion method employing ethylene glycol as a fuel. These catalysts have shown a relatively high activity in the total oxidation of naphthalene and, more importantly, a remarkable high selectivity towards CO₂. Different ethylene glycol concentrations (EG/Ce molar ratios from 0.5 to 1.5) have been used to optimize the preparation procedure. The optimal catalyst, that with a EG/Ce molar ratio of 0.75, exhibited the highest activity in the oxidative decomposition of naphthalene and, most importantly, a selectivity towards CO₂ of ca.100% over the range of temperature and consequently conversion. The high selectivity was postulated to be related to the high concentration of oxygen vacancies of the ceria catalyst.

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