

Nano-crystalline ceria catalysts for the abatement of polycyclic aromatic hydrocarbons

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Received 2 September 2005; accepted 6 September 2005

Nano-crystalline cerium oxide catalysts have been prepared by precipitation and evaluated for the total catalytic oxidation of naphthalene, which is a polycyclic aromatic hydrocarbon (PAH). Ceria synthesised by precipitation with urea was the most active catalyst for oxidation of naphthalene to carbon dioxide. The urea precipitated CeO_2 demonstrated over 90% naphthalene conversion to carbon dioxide at 175°C (100 ppm naphthalene, GHSV = 25,000 h^{-1}), whilst ceria precipitated via a carbonate only gave 90% conversion at 275°C. Comparison with known high activity total oxidation catalysts, Mn_2O_3 and 0.5% Pt/ $\gamma\text{-Al}_2\text{O}_3$, showed that the urea precipitated CeO_2 was a more effective catalyst for naphthalene total oxidation. At temperatures below those required to achieve catalytic activity the adsorption capacity of urea precipitated ceria for naphthalene was considerably greater than any of the other catalysts examined. The high adsorption capacity of the material provides the advantage that it can be used as a combined catalyst and adsorbent to remove PAHs from waste streams.

KEY WORDS: catalytic oxidation; ceria; naphthalene; PAHs; VOCs.

1. Introduction

In recent years environmental legislation has imposed increasingly stringent targets for permitted levels of atmospheric emission. Against this background, polycyclic aromatic hydrocarbons (PAHs) are an important family of environmental pollutants that are released to the atmosphere during the incomplete combustion, or the pyrolysis of organic material, and their emissions are mainly associated with the use of oil, gas, coal and wood in power generation [1]. Increased urban concentrations of PAHs are of particular concern because many of them show carcinogenic and/or mutagenic properties. PAH emissions, due to their high volatility and reactivity, can be released, not only supported onto particulate matter (PM) but also in the gas phase [2]. Whilst PAHs supported on PM can be trapped using treatment systems such as, cyclones, electrostatic precipitators and fabric filters; the control of gaseous PAH emissions are more difficult. Many different technologies have been developed for PAH abatement, but one of the most versatile is catalytic oxidation to carbon dioxide and water. Noble metal catalysts supported on Al_2O_3 , have been demonstrated to be the most active catalysts for the destruction of PAHs model compounds, mainly naphthalene [3]. However, the development of more active and cost-effective catalysts for complete oxidation of PAHs remains a major research target.

Cerium oxide (CeO_2) is a material that is recognised as having versatile properties as a catalyst [4]. In

particular, CeO_2 has demonstrated potential for the treatment of emissions, due to the ability to transport oxygen in combination with the ability to cycle easily between reduced and oxidized states (i.e. Ce^{3+} – Ce^{4+}) [5]. CeO_2 has also demonstrated potential for the removal of soot from diesel engine exhaust, the removal of organics from aqueous waste streams, additives for combustion catalysts [6], and in oxidative reactions [7]. Furthermore, considerable effort has focused on investigating the influence of ceria in established catalytic processes, such as fluid catalytic cracking and three-way-catalysts for vehicle emission control [5,6]. It has been observed that the catalyst performance is influenced strongly by the properties of the constituent CeO_2 particles. It has recently been shown that CeO_2 catalysts can be more active than noble metal catalysts in the catalytic combustion of a mono-aromatic compound, such as toluene [8]. Wang and Lin synthesised CeO_2 catalysts by four different methods, and found that CeO_2 catalysts prepared by a redox reaction with H_2O_2 showed the highest activity due to both a smaller crystallite size and a larger surface area. This catalyst was the only one more active than a noble metal catalyst. It has previously been demonstrated that the catalytic performance of several systems for the deep oxidation of alkanes and mono-aromatic compounds cannot be directly extrapolated to the total oxidation of PAHs [9]. To date there are no data available on the use of ceria catalysts for the oxidative destruction of PAHs.

Various synthesis techniques, based on wet chemical routes, have been employed for the preparation of CeO_2 nanoparticles. These methods include redox reaction [8],

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hydrothermal [10,11], reverse micelles [12], sonochemical [13], pyrolysis [14] and homogeneous precipitation methods [7,15–20]. Homogeneous precipitation is a relatively simple preparation route for formation of nanoparticles and it has the further advantage that it uses mild synthesis conditions. To the best of our knowledge, this is the first study not only showing the performance of CeO₂ catalysts in catalytic combustion of PAH, but also applying CeO₂ nano-ceria crystals prepared by a homogeneous precipitation method for the catalytic oxidation of volatile organic compounds. Herein we report details of the activity of nano-ceria crystals prepared by precipitation of cerium ammonium nitrate with urea in the abatement of PAH emissions.

2. Experimental

CeO₂ was prepared by a homogeneous precipitation method with urea as precipitating agent. The cerium salt used was (NH₄)₂Ce(NO₃)₆. Twenty g of the cerium salt was dissolved in 200 mL of deionised water and mixed with urea in a ratio of 1:3 (H₂N–CO–NH₂). The resulting solution was continuously stirred, whilst it was heated to 100°C. The resulting gel was boiled and aged for 24 h at 100°C. The final precipitate was collected by filtration. The solid obtained was dried at 120°C and calcined in static air at 400°C for 10 h. CeO₂ catalysts were also prepared by a precipitation method. An aqueous solution of the corresponding Ce-nitrate salt was stirred at 80°C. Aqueous sodium carbonate (0.25 M) was added dropwise until a pH of 8.2–9.0 was obtained. The resulting solution was stirred and aged for 1 h at 80°C. The paste obtained was filtered and washed several times with cold and then hot water to ensure the removal of chlorides and sodium cations. After drying in an oven at 120°C the catalysts were calcined in static air at 400°C for 3 h. Catalysts were characterised by powder X-ray diffraction, temperature programmed hydrogen reduction, scanning electron microscopy and nitrogen adsorption.

Catalyst activity 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 synthetic air. A total flow rate of 50 mL min⁻¹ was used and catalysts were packed to a constant volume to give a GHSV of 25,000 h⁻¹ for all studies. Analysis was performed by an on-line gas chromatograph with thermal conductivity and flame ionisation detectors. Catalytic activity was measured over the range 100–350°C in incremental steps, and temperatures were controlled by a thermocouple placed in the catalyst bed. Data were obtained at each temperature after naphthalene adsorption equilibrium was accomplished. After one hour of stabilisation time, three analyses were made at each temperature and average values were taken into account. The reaction temperature was increased and the same procedure followed to determine each data point.

3. Results and discussion

Table 1 shows the characterisation data of the ceria catalysts. The specific surface areas, determined by the BET method, and the assignments of the crystalline phases observed are summarised in table 1. It is observed that the preparation with urea of the CeO₂ showed an increase of the surface area (171 m² g⁻¹ vs. 86 m² g⁻¹). On the other hand, both CeO₂ samples presented the same Ce-containing crystalline phase, cubic fluorite. Figure 1 shows the XRD patterns for fresh and used sodium carbonate, CeO₂ (P) and urea CeO₂ (U), precipitated samples. The diffraction peaks occurred at 2θ = 28.5, 33.1, 47.5, 56.2 and 59.08, these are characteristic of the cubic fluorite structured CeO₂. The crystallite size for fresh and used samples are summarised in table 1. The catalysts prepared by carbonate precipitation showed a CeO₂ crystal size, 5.2 nm, slightly higher than the one prepared by the urea method, 4.7 nm. It was observed that the ceria crystal size did not significantly change after ceria was used for naphthalene catalytic combustion. Whilst crystal particle size slightly decreased for CeO₂ (P), from 5.2 to 4.9 nm, a slight increase was observed in the case of CeO₂ (U), from 4.7 to 5.0 nm. However, this slight change did not affect the long-term activity of the Ceria catalysts. Table 1 also

Table 1
Characteristics of CeO₂ catalysts

Catalysts	Surface area ^a (m ² g ⁻¹)	Crystal phases ^b	Particle size ^b (nm)	H ₂ consumption ^c (μmoles g _{cat} ⁻¹)	FWHM ^d (cm ⁻¹)	NRE100 ^e (min)
CeO ₂ (P)	87	Cubic fluorite	5.2	715	36	< 20
CeO ₂ (U)	171	Cubic fluorite	4.7	638	37	210
CeO ₂ (H ₂ O ₂)	79	Cubic fluorite	9.2	550	29	< 20

^aCalculated by the BET method.

^bBy XRD analysis.

^cBy TPR analysis, 100 mg sample, 50 mL min⁻¹ H₂, 10°C min⁻¹.

^dFull width at half maximum of the CeO₂ line in the Raman spectra.

^eNaphthalene adsorption efficiency at 100°C: Time without detecting naphthalene in the outlet catalytic reactor gases. Space velocity: 25,000 h⁻¹.

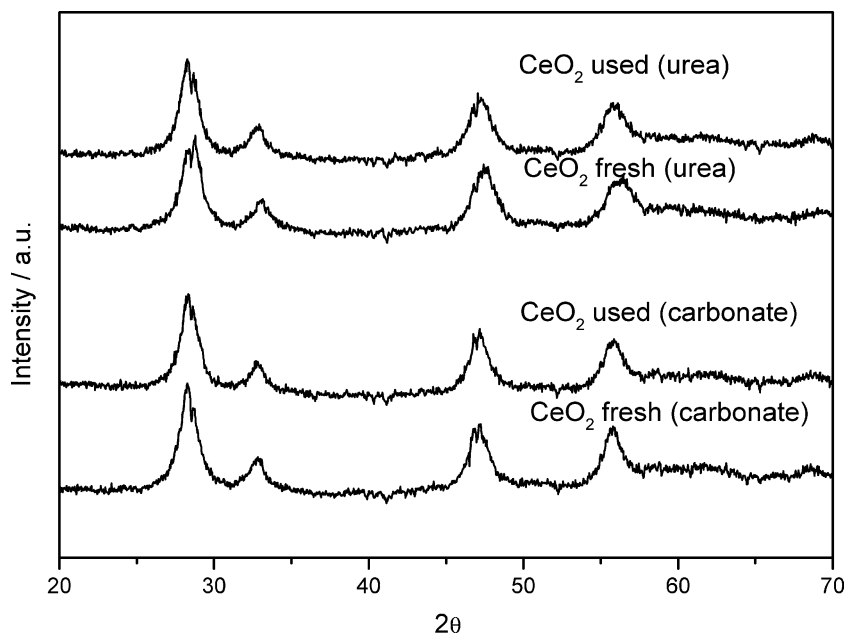


Figure 1. Powder X-ray diffraction patterns of fresh and used CeO_2 catalysts.

shows the full width at half maximum (FWHM) of the characteristic Raman bands of ceria at $462\text{--}464\text{ cm}^{-1}$. It has been reported that these values can be correlated with both the average crystal size of ceria and the defect concentration in the ceria structure [21]. Comparing the FWHM values of the two ceria catalysts, it is seen that both materials show approximately the same value. Therefore, since XRD data showed a similar particle size for both catalysts, the number of oxygen vacancies in the ceria surface was not affected by the precipitation

method used to produce the ceria catalysts. Finally, a slight decrease (4 cm^{-1}) in the FWHM values of ceria catalysts was observed after reaction. This fact could be linked with less oxygen vacancies in ceria, probably because of the enhanced ceria surface layers re-oxidation [21], since the ceria crystal particle size did not significantly change after reaction.

TPR profiles of the two different ceria samples are shown in figure 2. It can be observed that whilst CeO_2 (U) began to reduce around 300°C , CeO_2 (P) showed

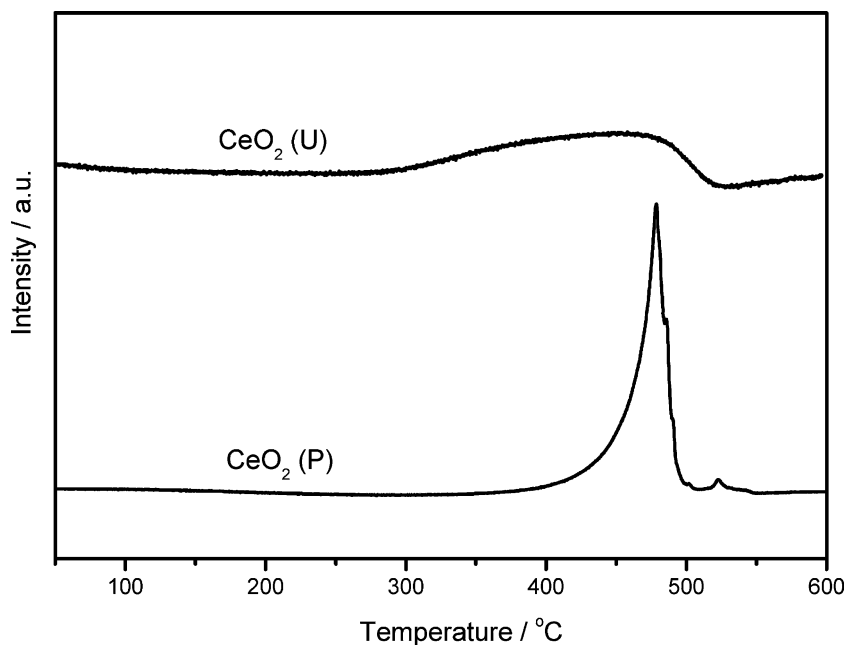


Figure 2. TPR profiles of CeO_2 catalysts.

an onset temperature around 350°C. Moreover, whilst a very broad peak with a maximum at 457°C was registered for CeO₂ (U), in the case of CeO₂ (P), the reduction peak was very sharp with a maximum at 480°C. This reduction peak for both catalysts was assigned to the reduction of the surface capping oxygen in the CeO₂ [22], as the reduction of bulk ceria only occurs at temperatures higher than 750°C [21]. It can be concluded that the homogeneous precipitation with urea leads to a decrease in the reduction temperature of the surface ceria layers. The total hydrogen consumption of the ceria catalysts is reported in table 1. It can be seen that this amount was marginally larger for the CeO₂ (P) sample than for CeO₂ (U), which might be due to subtle different surface structures formed during preparation by the carbonate and urea precipitation techniques [23]. Figure 3 shows the SEM images of fresh and used CeO₂ catalysts prepared by precipitation with carbonate or urea. In this figure, it can be observed that both fresh catalysts show a similar morphology, consisting of conglomerates of spherical particles. However, a different morphology can be observed between both catalysts after reaction with naphthalene. Whilst CeO₂ (P) particle morphology remained practically unchanged, CeO₂ (U) changed from agglomerates of spherical particles to a prismatic form. The presence of defects in these prismatic forms, where naphthalene molecules could be adsorbed could explain the very high naphthalene removal efficiency observed for this catalyst (table 1).

The yield to CO₂ for the catalytic oxidation of naphthalene over CeO₂ (U) and CeO₂ (P) catalysts are presented in figure 4. For comparative purposes, the catalytic activities of CeO₂ (H₂O₂) prepared by a redox reaction with H₂O₂ according to ref. [8], Mn₂O₃ and 0.5% Pt/γ-Al₂O₃ are also shown. The main characteristics of CeO₂ (H₂O₂) are also reported in table 1. The reason for using the CO₂ yield is that naphthalene is a polyaromatic molecule, which can easily be adsorbed onto the surface of high surface area materials, which may lead to over estimation of catalytic oxidation activity [24]. Moreover, it should be taken into account that the use of total naphthalene conversion may also lead to erroneous conclusions due to the formation of by-products [3]. Therefore, the conversion to CO₂ and not the total conversion of naphthalene, is used to establish the catalytic activity. It is showed in figure 4 that whilst CeO₂ (U) has the highest catalytic activity, CeO₂ (P) was the least active catalyst at all the temperatures. Above 175°C the CO₂ yield and naphthalene conversion over CeO₂ (U) was identical, demonstrating that no by-products were formed above 175°C. CeO₂ (H₂O₂) was less active than CeO₂ (U) and showed comparable activity to an Mn₂O₃ catalyst. The low activity of CeO₂ (P) could be due to the presence of surface carbonate species, which could poison the ceria active sites (corroborated by TGA analysis). It was observed that CO₂ yields of about 10% were reached around 115°C, and 240°C over the CeO₂ (U) and CeO₂ (P) catalysts, respectively. On the other hand, this

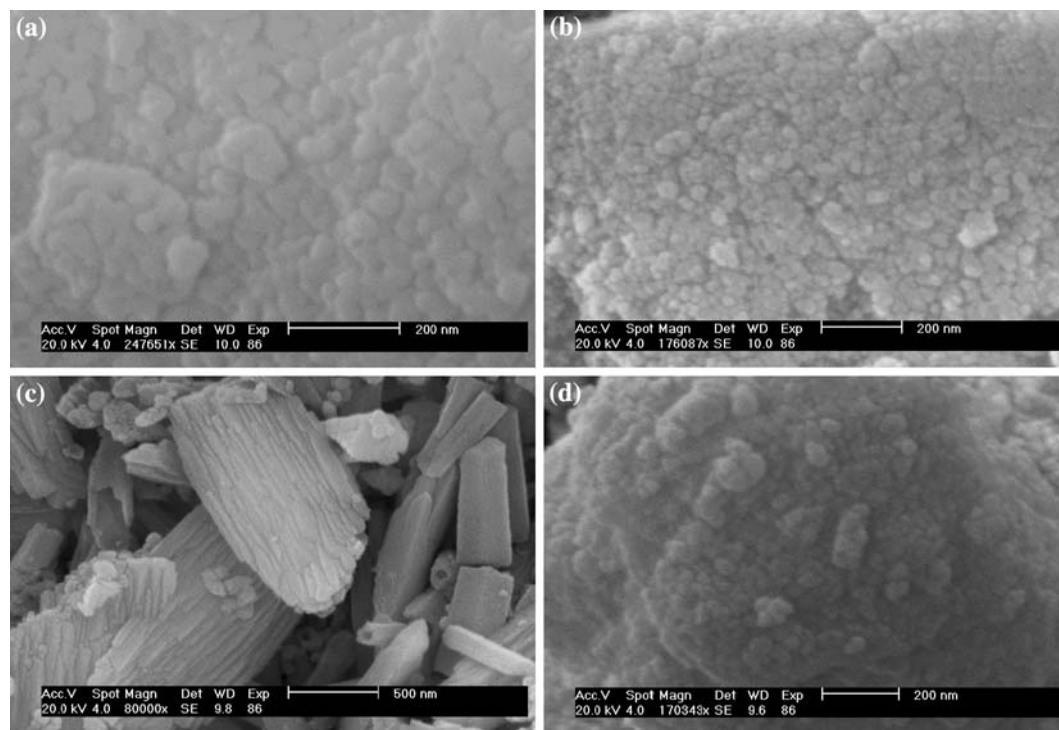


Figure 3. SEM images of fresh and used CeO₂ catalysts. (a) fresh-CeO₂ (urea); (b) fresh-CeO₂ (carbonate); (c) used-CeO₂ (urea); and (d) used-CeO₂ (carbonate).

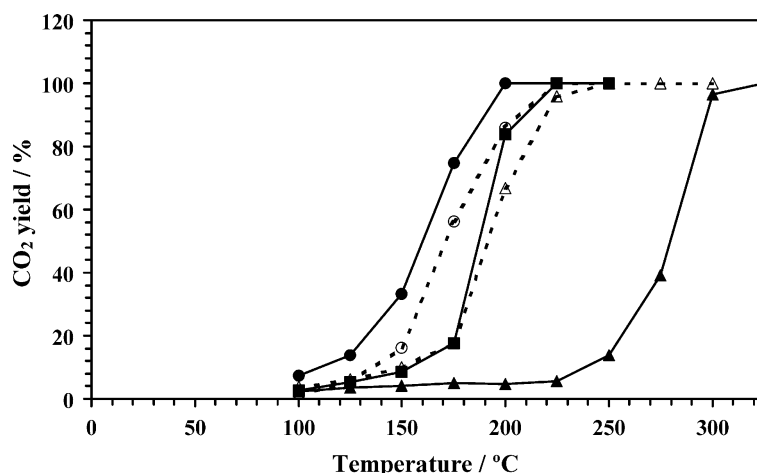


Figure 4. Comparison of catalytic activities of metal oxide catalysts and noble metal catalysts for the combustion of naphthalene. (line) ● CeO₂ (urea) ; ■ CeO₂ (H₂O₂), ▲ CeO₂ (carbonate); (dash line) ○ 0.5% Pt/γ-Al₂O₃, △ Mn₂O₃.

conversion to CO₂ was reached around 140°C over Pt/γ-Al₂O₃ and around 150°C over Mn₂O₃ and CeO₂ (H₂O₂) catalysts. It was also evident (figure 4) that conversions of 90% were obtained around 175°C, 210°C, 290°C and 220°C over the four different metal oxide catalysts, CeO₂ (U), CeO₂ (H₂O₂), CeO₂ (P) and Mn₂O₃ catalysts and around 210°C over the noble metal catalyst. Therefore, CeO₂ prepared by the urea precipitation method was remarkably more active than the other catalysts tested in this work. Furthermore, total conversion to CO₂ was reached at a much lower temperature than for the noble metal catalyst. However, it can also be observed that although CeO₂ (H₂O₂) has been reported to be more active than a noble metal catalyst in toluene incineration, this catalyst was less active than the noble metal reported in this study, 0.5%Pt/γ-Al₂O₃. This fact agrees with the conclusion previously found by this research group, showing that the performance of a catalytic system in the combustion of mono-aromatic compounds cannot be extrapolated to the total oxidation of polyaromatic compounds. We consider that the main reason for the high activity of CeO₂ (U) catalyst is linked to a smaller crystallite size, higher surface area and formation of a more active surface structure.

It is clear that CeO₂ (U) is a very active catalyst for the oxidation of naphthalene at relatively low temperatures. It is also important to consider the ability of the material to remove naphthalene by adsorption at temperatures below which the catalyst is active. To probe the naphthalene removal efficiency by adsorption at 100°C, NRE100 was determined. NRE100 is the time needed to detect naphthalene in the outlet gases of the catalytic reactor at 100°C over a fresh sample of the catalyst. In table 1, it can be observed that whilst CeO₂ (U) shows a remarkably high value of NRE100, at 100°C, the adsorption capacity in the case of CeO₂ (P) and CeO₂ (H₂O₂) was lower than 20 min at the same gas hourly space velocity (GHSV). The NRE100 for CeO₂

(U) was also around 4–5 times greater than in the case of Pt/γ-Al₂O₃ and Mn₂O₃ catalysts. The NRE100 value per mass of catalyst for CeO₂ (U) was around 2 times higher than for Pt/γ-Al₂O₃ and around 3 times that for Mn₂O₃ catalysts. However, CeO₂ (U) showed a comparable BET surface area to Pt/γ-Al₂O₃ (175 m² g⁻¹) and approximately twice that of CeO₂ (P) and Mn₂O₃ (78 m² g⁻¹). Therefore, the improvement in the NRE100 was not a simple function proportional to surface area. It is apparent that the high adsorption capacity of CeO₂ (U) is also dependant on the structure. This may be manifested as a surface structure that presents a greater number of surface sites for naphthalene adsorption. Moreover, urea precipitation may also lead to a textural structure with an appropriate pore size distribution providing greater access to the surface where naphthalene molecules can be adsorbed. This effect cannot be achieved by the other preparation methods. All these factors show that CeO₂ nano-crystals prepared by a homogeneous precipitation methods with urea are very relevant catalysts for PAHs removal, not only a temperature higher than 200°C, but also during the cold-start process of the catalytic system when the CeO₂ catalysts can work as a very efficient PAH adsorbent.

The performance of CeO₂ (U) catalyst for the naphthalene destruction efficiency has been evaluated in the temperature range of 100–250°C in three consecutive cycles and as a function of time on stream for a period of 60 h at 200°C. Whilst the catalytic performance remained unchanged throughout the three cycles, the NRE100 increased in the second and third cycle by a factor of 1.5, and this was most likely due to the cleaning of the ceria surface. Hundred percentage of naphthalene conversion to CO₂ was reached during the time on stream study. Further work on the long-term use of these catalysts is still underway to determine the total catalyst lifetime. However, these data demonstrate that the catalytic activity is stable through a temperature

Table 2
Comparison of naphthalene catalytic activity for different catalysts

Catalyst	T10 (°C)	T50 (°C)	T90 (°C)	GHSV (h ⁻¹)	Reference
CeO ₂ (urea)	110	160	190	25,000	This work
Pt/Al ₂ O ₃	135	170	210	25,000	
Pt/Al ₂ O ₃ ^a	169	185	202	25,000	[27]
Pt/Al ₂ O ₃ ^b	194		203	20,000	[3]
Pd/Al ₂ O ₃ ^b	197		206	20,000	
Pt/Al ₂ O ₃ ^c	194	204	310	20,000	[28]
Cu/Mn/Al ₂ O ₃ ^c	180	207		20,000	
2.0% Pd/HZSM-5 ^d		156		20,000	[29]
0.3% Pt/Silica fibre ^d	186	209	233	20,000	[30]
1.2% Pd-Zr-Yzeolite ^d		135		20,000	[31]
CuO-Pd/La-Al ₂ O ₃ ^e		270		23,000	[32]

^a600 ppmv naphthalene, 20.95 vol.% O₂, conversion in terms of CO₂ yield.

^b100 ppmv naphthalene, 10 vol.% O₂, conversion in terms of CO₂ yield.

^c50 ppmv naphthalene, 200 ppmv CH₄, 2550 ppmv CO, 12 vol.% CO₂, 10 vol.% O₂, 0–20 vol.% H₂O, conversion in terms of C₈H₁₀ destruction.

^d50 ppmv naphthalene, 200 ppmv CH₄, 2500 ppmv CO, 12 vol.% CO₂, 10 vol.% O₂, 12 vol.% H₂O, conversion in terms of C₈H₁₀ destruction.

^e50 ppmv naphthalene, 200 ppmv CH₄, 2550 ppmv CO, 12 vol.% CO₂, 10 vol.% O₂, 13.5 vol.% H₂O, conversion in terms of C₈H₁₀ destruction.

cycle. This is important when considering the mode of PAH removal in a treatment process. The combination of a high adsorption capacity with high oxidation efficiency to CO₂ provides the capability to operate at low temperatures to remove PAHs by adsorption, followed by an increase of the temperature to oxidise the surface-bound species. Such a process offers the economic advantage of lower fuel costs, as the catalyst need not be maintained at elevated temperatures permanently. The combination of adsorption/catalytic oxidation has been identified as an important technology for Environmental Protection [25], and identification of suitable adsorbents/catalysts are critical [26].

Table 2 compares the temperatures of naphthalene removal for different conversions, T10 (X10%), T50 (X50%) and T90 (X90%) over several catalysts tested in this study and in the literature [3,27–32]. From table 2, CeO₂ nano crystals prepared by a homogeneous precipitation method with urea are markedly more active than noble metal catalysts, except for palladium-modified zeolites. Against this background, it is worth commenting that the naphthalene catalytic activity of the modified-zeolites was measured in terms of naphthalene conversion. Thus, overall results may lead to erroneous conclusions due to the formation of reaction by-products [3]. For example, T50 in terms of naphthalene conversion for CeO₂ (U) catalyst was reached at 130°C, 5°C lower temperature than over a 1.2%Pd–Zr-modified Y zeolite.

4. Conclusions

In summary, we have reported the preparation of a CeO₂ nanoparticle catalyst with an exceptionally high PAH elimination efficacy. During a cold-start process, or cyclic temperature operation, CeO₂ can act as an adsorbent/catalyst material for PAHs removal. Then,

when heated to higher temperature, ca. 200°C, it acts as a very efficient total oxidation catalyst for PAHs. The high activity and simple preparation method used to produce these catalysts makes them interesting and worthy of further study. The ceria catalyst appears to be appropriate for the hot gas cleaning of PHAs from gas exhaust in power generation systems and other similar applications for protection of the environment from harmful emissions.

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