

Article

Effect of Morphology-Dependent Oxygen Vacancies of CeO₂ on the Catalytic Oxidation of Toluene

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Abstract: Catalytic oxidation is regarded as an effective, economical, and practical approach to remove volatile organic compounds such as important air pollutants. CeO₂ catalysts with different morphologies exhibit different oxygen vacancies content, which plays a vital role in oxidation reaction. Herein, three distinct morphologies of CeO₂ i.e., shuttle (CeO₂ (S)), nanorod (CeO₂ (R)), and nanoparticle (CeO₂ (P)), were successfully fabricated by the SEM and TEM results, and investigated for toluene catalytic oxidation. The various characterizations showed that the CeO₂ (S) catalyst exhibited a larger surface area along with higher surface oxygen vacancies in contrast to CeO₂ (R) and CeO₂ (P), which is responsible for its excellent toluene catalytic oxidation. The 90% toluene conversion temperature at 225 °C over CeO₂ (S) was less than that over CeO₂ (R) (283 °C) and CeO₂ (P) (360 °C). In addition, CeO₂ (S) showed a greater reaction rate ($14.37 \times 10^{-2} \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$), TOF_{ov} ($4.8 \times 10^{-4} \cdot \text{s}^{-1}$) at 190 °C and lower activation energy value (67.4 kJ/mol). Furthermore, the CeO₂ (S) also displayed good recyclability, long-term activity stability, and good tolerance to water. As a result, CeO₂ (S) is considered a good candidate to remove toluene.

Keywords: toluene; CeO₂; distinct morphologies; catalytic oxidation; oxygen vacancies



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1. Introduction

VOCs (volatile organic compounds) released from different industries as well as transportations producing photochemical haze, ground-level ozone, photochemical smog and organic aerosol precursors are polluting the air [1,2]. Toluene, used in different industries, is creating a severe danger to both the atmosphere and human life [3]. Today, toluene abatement is the utmost priority due to its high emission and stable nature. Therefore, finding an efficient method to eliminate toluene is very important. Among various methods to remove toluene [4], catalytic oxidation is regarded as an effective, economical, and practical approach [4]. In catalytic oxidation of toluene, catalysts made of precious and non-precious metals have both been broadly examined. Generally, catalysts made of precious metals are chosen because they are highly active in low-temperature VOCs abatement [5]. However, the expensive nature, aggregation and easy sintering limits the practical applications of precious metal-based catalysts [6]. Therefore, catalysts made of non-precious metals are preferred due to their low cost and excellent VOCs oxidation activity [7,8].

Among different non-precious metal catalysts, CeO₂ is considered as an effective catalyst due to its excellent reducibility between Ce³⁺/Ce⁴⁺, oxygen storage capacity, and rich oxygen vacancies. [9,10]. Distinct morphologies of CeO₂ offer different catalytic activities, indicating a good relation between morphology and catalytic activity [11]. The different morphologies of CeO₂ may affect the oxygen storage capacity, reducibility, and oxygen vacancy formation [11]. The previous studies [11–15] revealed that different morphologies of CeO₂ catalysts were beneficial for oxidation performance by providing new physiochemical properties, for instance: high Ce³⁺ concentrations, reducibility and oxygen vacancies,

etc. For example, between CeO₂ nanoparticles, nanocubes and nanorods, CeO₂ nanorods showed the best activity because of abundant oxygen vacancies and higher reducibility [12]. Similarly, the effect of CeO₂ nanorods, nanocubes, and hollow sphere morphologies investigation was also conducted on the toluene catalytic oxidation [13], and the CeO₂ with hollow sphere morphology showed excellent catalytic oxidation performance owing to the bigger surface area, higher Ce³⁺ content, and higher oxygen vacancies on its surface. In addition, CeO₂ hierarchical microspheres exhibited supreme toluene oxidation activity, because of the higher surface area and plentiful oxygen vacancies compared to non-hierarchical CeO₂ microspheres [14]. In the same way, ultrasonic-assisted CeO₂ nanorods were fabricated for the abatement of toluene through oxidation. It was concluded that CeO₂ with fine shape nanorods showed higher oxidation activity and that critical factors for the formation of CeO₂ nanorods are sodium hydroxide concentration, cerium precursors, and ultrasonic employments [15]. Thus, it is essential and important to develop a CeO₂ catalyst with distinct morphologies and investigate these morphologies for oxidation of toluene.

Herein, three CeO₂ distinct morphology (shuttle, nanorod, and nanoparticle) catalysts were hydrothermally synthesized. The XRD (X-ray diffraction), BET (Brunauer-Emmett-Teller), SEM (scanning electron microscopy) and TEM (transmission electron microscopy) were utilized to examine the crystallinity, surface area, and morphologies of three CeO₂ catalysts. Moreover, surface oxygen vacancies concentration was determined by Raman, XPS (X-ray photoelectron spectroscopy), hydrogen reduction and oxygen desorption temperature-programmed (H₂-TPR & O₂-TPD) analysis. The characterization findings were used to explore the correlation between toluene catalytic oxidation and CeO₂ morphologies.

2. Result and Discussion

2.1. Bulk Structure Analysis

The structure of the crystal and crystallite size of all three samples were tested through XRD. As displayed in Figure 1a, all three catalysts exhibit well-defined diffraction planes at $2\theta = 28, 33, 47, 56, 59, 69, 77$ and 79° , that were attributed to (111), (200), (220), (311), (222), (400), (331), and (420) planes, correspondingly (PDF # 34-0394). The diffraction planes of CeO₂ (S) are far broader and weaker as compared to CeO₂ (R) and CeO₂ (P), suggesting that the lattice is more distorted in CeO₂ (S) [16,17]. The crystallite sizes of all three catalysts were measured based on the most prominent plane (111) with the help of the Scherrer formula. The crystal size of CeO₂ (S) (9 nm) is less compared to CeO₂ (R) (11 nm) and CeO₂ (P) (12 nm), listed in Table 1. To evaluate the textural properties (surface area), the isotherms of N₂ adsorption-desorption were assessed (Figure 1b). Each catalyst displays isotherms of type IV with definite H3 type hysteresis loops. The pore size distribution (inset of Figure 1b) shows the presence of a number of nanopores (2–5 nm) in CeO₂ (S), suggesting its high surface porosity, which is due to loss of polymer molecules and the conversion process into CeO₂. The determined surface areas for CeO₂ (S), CeO₂ (R), and CeO₂ (P) are 116, 79 and 60 m²·g^{−1}, respectively, and the pore volumes are 0.54, 0.49 and 0.09 cm³·g^{−1}, correspondingly (Table 1), demonstrating that CeO₂ (S) has a much higher surface area.

The three CeO₂ catalyst structures were probed by using Raman spectroscopy. As displayed in Figure 2, these catalysts show three bands at 256, 461, and 600 cm^{−1}. The band at 256 cm^{−1} is allocated to CeO₂ second-order transverse acoustic (2TO) mode, the strong band at 461 cm^{−1} belongs to the F_{2g} triply degenerate mode, and the defect-induced (D) band detected at 600 cm^{−1} is linked with the generation of oxygen vacancies due to Ce³⁺ presence in CeO₂ [18–21]. The CeO₂ (S), CeO₂ (R), and CeO₂ (P) oxygen vacancies estimation can be interpreted by integrating the band area ratio (A_{600}/A_{461}) of 600 cm^{−1} to 461 cm^{−1} [14]. CeO₂ (S) has a higher A_{600}/A_{461} ratio (0.62) compared to CeO₂ (R) (0.23), and CeO₂ (P) (0.16), suggesting it has more oxygen vacancies than CeO₂ (R) and CeO₂ (P) (Table 1).

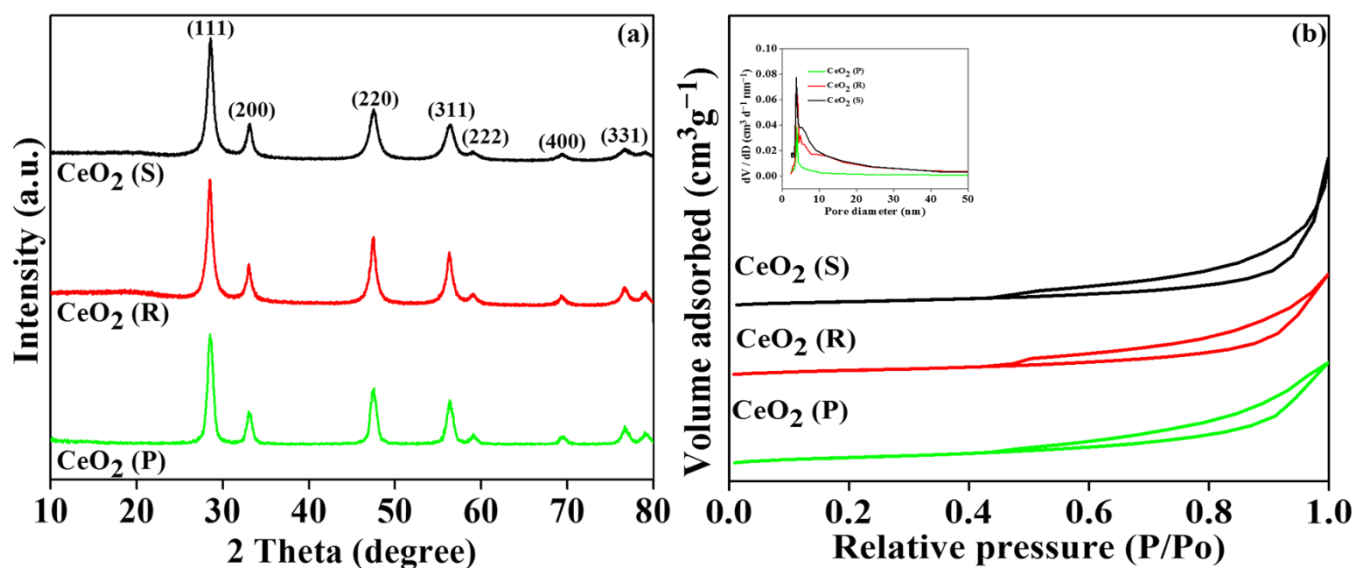


Figure 1. XRD patterns (a) and N₂ adsorption–desorption isotherms, BJH pore distribution (inset) (b) of CeO₂ (S), CeO₂ (R) and CeO₂ (P).

Table 1. The XRD, BET, Raman and XPS results of CeO₂ (S), CeO₂ (R) and CeO₂ (P).

Samples	Crystallite Size (nm) ^a	BET Surface Area (m ² ·g ⁻¹) ^b	Pore Size (nm) ^b	Pore Volume (cm ³ ·g ⁻¹) ^b	A ₆₀₀ /A ₄₆₁ ^c	Ce ³⁺ /(Ce) ^d (%)	O _β /(O) ^e (%)
CeO ₂ (S)	9	116	3.85	0.54	0.62	39.6	55.4
CeO ₂ (R)	11	79	3.72	0.43	0.23	31.4	48.3
CeO ₂ (P)	12	60	3.98	0.09	0.16	23.8	45.2

^a. Crystallite size calculated by XRD using Scherrer equation. ^b. Measured from N₂ adsorption–desorption isotherms. ^c. Calculated from the integrated peak areas centered at 600 and 461 cm⁻¹ of the Raman spectra. ^d. Ratio of Ce³⁺ to (Ce³⁺ + Ce⁴⁺). ^e. Ratio of O_β to (O_α + O_β).

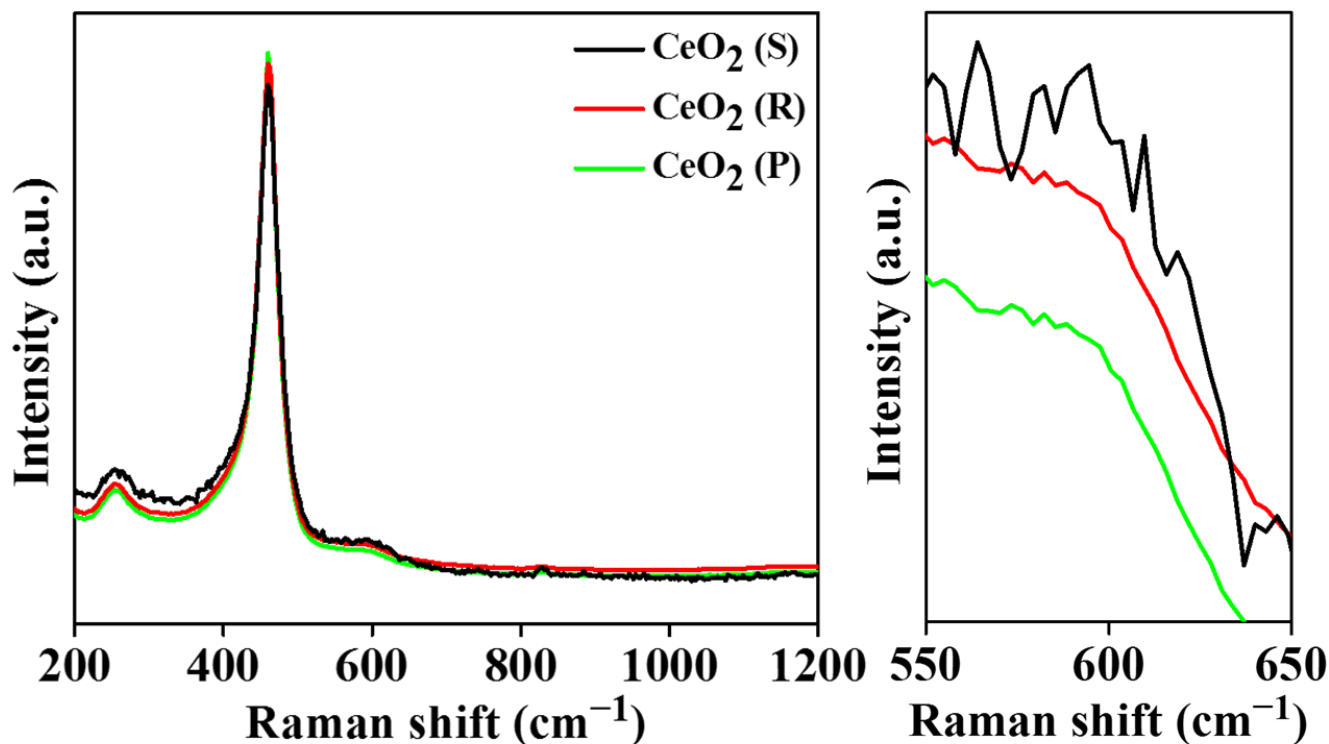


Figure 2. Raman spectra of CeO₂ (S), CeO₂ (R) and CeO₂ (P).

2.2. SEM and TEM Analysis

The catalyst morphologies were analyzed through SEM and TEM (Figure 3). The SEM image (Figure 3a,b) of CeO_2 (S) exhibits shuttle-like morphology that is evenly distributed with 1.2 μm average diameter and 6.2 μm average length. The TEM images (Figure S1) indicate that the shuttle-like morphology CeO_2 (S) comprises various nanorods which are orientationally attached, resulting in the formation of shuttle morphology; dense nanopores in the orientationally attached nanorods can also be observed (Figure S1b). For the CeO_2 (R) sample (Figure 3c,d)), nanorod morphology is observed with 7.7 and 83 nm average diameter and length, respectively. Figure 3e,f) displays the CeO_2 (P) nanoparticle morphology with an average particle size of 12 nm. These findings suggest the successful formation of different morphologies derived from different preparation methods. Furthermore, the HRTEM image of CeO_2 (S), CeO_2 (R), and CeO_2 (P), shown in Figure 3h and Figure S2, exposes (111), (200) and (220) crystal planes with 0.31, 0.27 and 0.19 nm interplanar crystal spacing of CeO_2 . Besides, numerous crystal defects and distortions exist in CeO_2 (S) and are marked with a yellow rectangle and white circle (Figure 3h), respectively. This also indicates that there is a great number of surface oxygen vacancies in CeO_2 (S) [14,22,23].

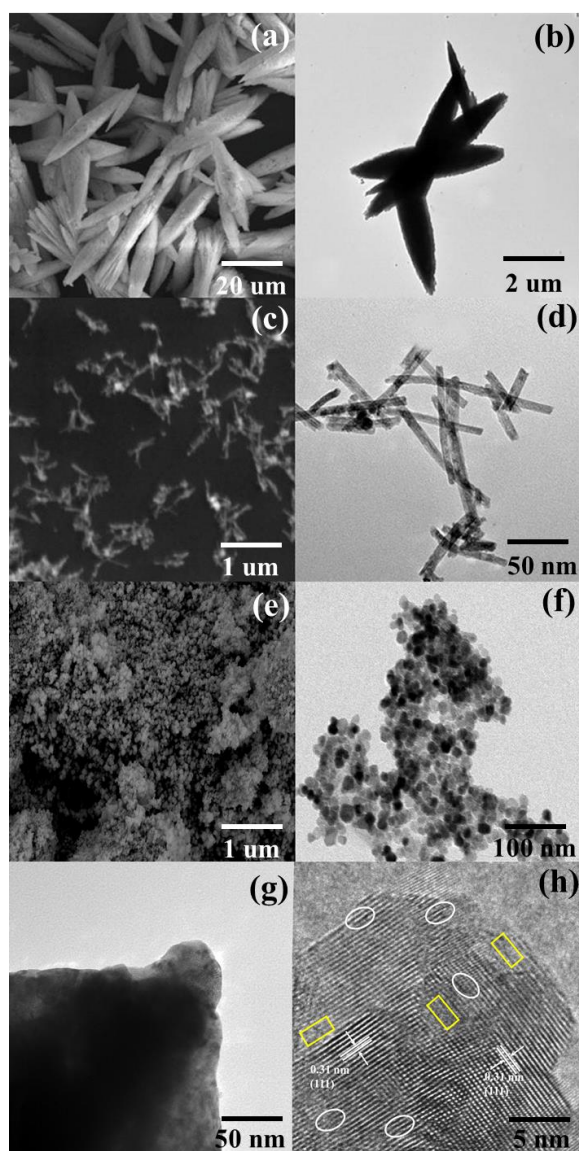


Figure 3. SEM and TEM images of CeO_2 (S) (a,b), CeO_2 (R) (c,d) CeO_2 (P) (e,f) and HRTEM image of CeO_2 (S) (g,h).

2.3. H₂-TPR and O₂-TPD Analysis

H₂-TPR was used to examine the CeO₂ (S), CeO₂ (R), and CeO₂ (P) reducibility. As presented in Figure 4a, three distinct morphology catalysts show two temperature reduction peaks at regions below and above 550 °C designated as regions I and II, which are credited to species of surface and lattice oxygen, correspondingly. The region I reduction peak includes surface adsorbed oxygen and subsurface oxygen [24,25]. For CeO₂ (S) and CeO₂ (R), there is an obvious shoulder reduction peak at about 370 °C compared with CeO₂ (P), which can be attributed to surface adsorbed oxygen reduction upon oxygen vacancy. Moreover, the initial reduction temperature of the peak in region I for CeO₂ (S) is at about 230 °C, which is lower compared to CeO₂ (R) (~280 °C) and CeO₂ (P) (~340 °C). Furthermore, along with low reduction temperature, the CeO₂ (S) also presents a wide reduction peak in region I with a consumption value of H₂ of 595.4 µmol·g⁻¹ followed by CeO₂ (R) (362.4 µmol·g⁻¹) and CeO₂ (P) (278.3 µmol·g⁻¹). The above results indicate the reducibility and the quantity of surface adsorbed oxygen decrease as follows: CeO₂ (S) > CeO₂ (R) > CeO₂ (P), signifying the CeO₂ (S)'s strongest oxidation ability.

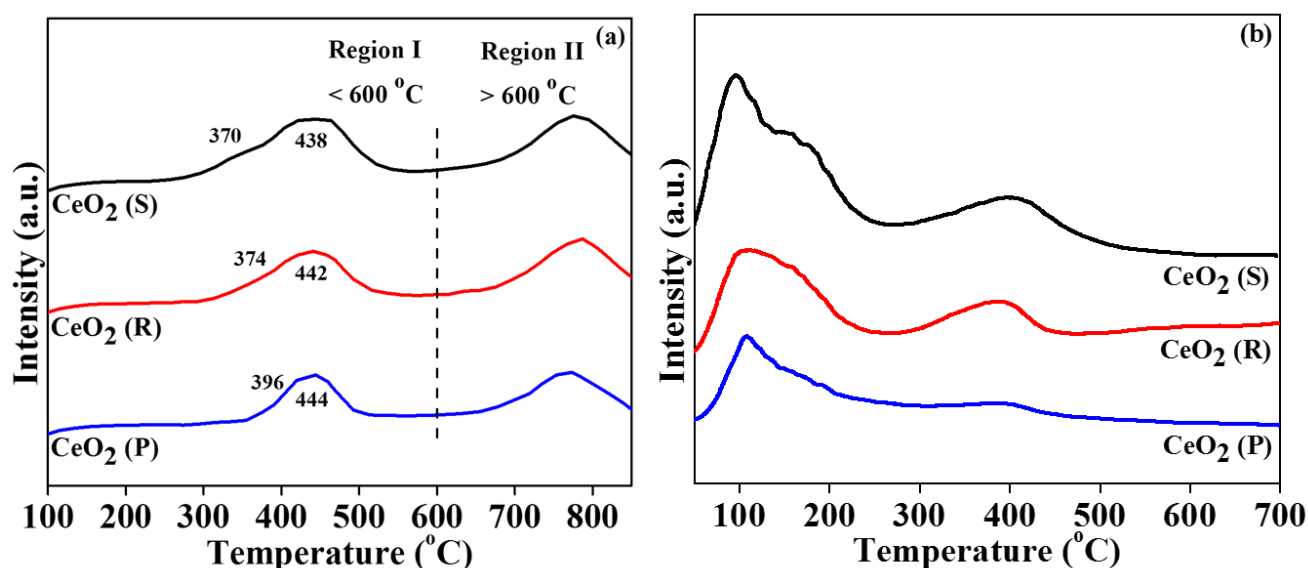


Figure 4. H₂-TPR (a) and O₂-TPD (b) profiles of CeO₂ (S), CeO₂ (R) and CeO₂ (P).

The desorption capacity of oxygen species of catalysts was investigated by O₂-TPD. As displayed in Figure 4b, two desorption peaks are observed below 550 °C for the catalysts. Typically, the desorption peak below 280 °C is assigned to the species of surface adsorbed oxygen (O₂⁻ and O⁻) and a peak between 280–550 °C is allocated to the surface lattice oxygen species (O²⁻) [26–28]. The area of desorption peak was used to calculate the quantity of surface adsorbed oxygen. The quantity is higher on CeO₂ (S) (303.3 µmol·g⁻¹) than on CeO₂ (R) (133.4 µmol·g⁻¹) and CeO₂ (P) (113.4 µmol·g⁻¹). Hence, it might be concluded that CeO₂ (S) has abundant surface oxygen vacancies that allow it to generate more species of surface adsorbed oxygen and is aligned well with the findings of H₂-TPR.

2.4. XPS Analysis

The three CeO₂ catalysts surface chemical states were investigated by XPS (Figure 5). As presented in Figure 5a, the Ce 3d XPS spectrum was resolved into eight peaks. The six peaks represented as V, V', V'', U, U' and U'' belong to the Ce⁴⁺ species and the remaining peaks denoted as V' and U₀ are considered as Ce³⁺ species [29,30]. The presence of Ce³⁺ indicates the surface oxygen vacancies generation; therefore, the ratio of Ce³⁺/(Ce³⁺ + Ce⁴⁺) was calculated. The percentage of Ce³⁺ species listed in Table 1 is 39.6%, 31.4%, and 23.8% on CeO₂ (S), CeO₂ (R), and CeO₂ (P), respectively. The higher amount of Ce³⁺ species on CeO₂ (S) reveals that its surface has many oxygen vacancies. O 1s XPS spectrum

(Figure 5b) was resolved into three distinct peaks. These three peaks at 529.8, 531.6, and 533.0 eV denoted as O_α , O_β , and O_γ are attributed to species of surface lattice oxygen, surface adsorbed oxygen, and adsorbed H_2O , respectively [8]. The generation of surface adsorbed oxygen points to the existence of oxygen vacancies; therefore, $O_\beta/(O_\alpha+O_\beta)$ ratio was calculated to find the content of oxygen vacancies [25]. As listed in Table 1, the CeO_2 (S) (55.4%) has high oxygen vacancies concentration in contrast to CeO_2 (R) (48.3%) and CeO_2 (P) (45.2%).

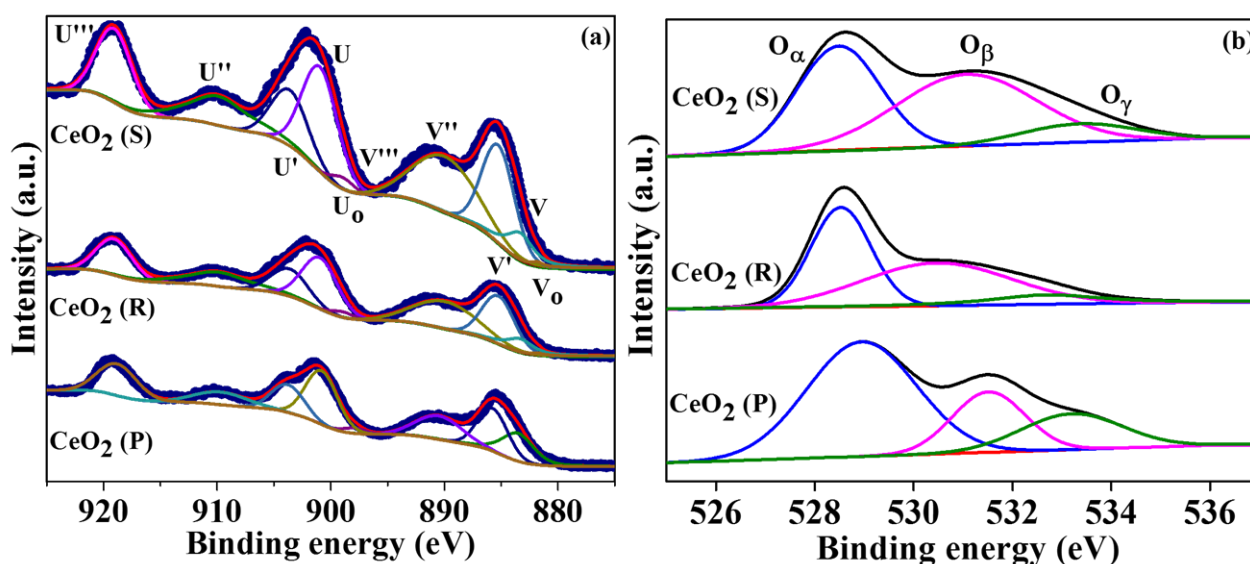


Figure 5. XPS spectra of (a) Ce (3d) and (b) O (1s) of CeO_2 (S), CeO_2 (R) and CeO_2 (P).

2.5. Catalytic Oxidation Activity

The toluene catalytic oxidation activity was evaluated for CeO_2 (S), CeO_2 (R), and CeO_2 (P) catalysts. Figure 6a reveals that the CeO_2 (S) offers excellent activity with 50% and 90% toluene conversion at low temperatures of (T_{50}) 208 and (T_{90}) 225 °C, respectively. The CeO_2 (R) and CeO_2 (P) show T_{50} is 231 and 283 °C, respectively, and the corresponding T_{90} is 324 and 360 °C (Table 2). This indicates that CeO_2 with different morphologies can offer different catalytic activity, and shows the excellent activity of CeO_2 (S) with special shuttle-like morphology. In addition, as shown in Figure 6b, the toluene oxidation for five consecutive cycles was investigated, and it was found that there is no decrease in catalytic oxidation performance, suggesting its strong recyclability of oxidation activity.

The catalytic activity stability of CeO_2 (S) in terms of time was also evaluated under 90% conversion of toluene, and there was no obvious loss in the conversion of toluene after 40 h (Figure 6c). Moreover, no decrease in the lower toluene conversion (50%) was observed over CeO_2 (S) in 20 h, as presented in Figure 6c (inset). Therefore, it can be deduced that CeO_2 (S) possesses excellent catalytic activity stability under both lower and higher conversion of toluene.

Generally, water imparts a negative effect on the catalyst performance, so investigating the catalytic performance in the presence of water is very necessary. As illustrated in Figure 6d, the toluene conversion (90%) remains unchanged for 5 h at 225 °C in the absence of H_2O . After inducing 3 vol% H_2O in the feed, the toluene conversion decreases to 87% and decreases further to 84% with the higher H_2O amount (5 vol%) in the feed. Interestingly, when the water is removed from the feed, the conversion of toluene can recover to 90%, elucidating a great tolerance to water for the CeO_2 (S) catalyst.

The rate of reaction of three CeO_2 samples was estimated with the help of Equation (2). The results displayed in Figure 7a and Table 2 suggest that the reaction rate increases as CeO_2 (S) > CeO_2 (R) > CeO_2 (P), which also confirms that in the toluene catalytic oxidation, CeO_2 (S) is the most efficient catalyst. Furthermore, the oxygen vacancy concentration-

based turnover frequency (TOF_{ov}) of CeO_2 catalysts was determined by using Equation (3) as shown in Figure 7b. The TOF_{ov} value at 170, 180, and 190 °C for the three catalysts increases as follows: CeO_2 (S) > CeO_2 (R) > CeO_2 (P) (Table 2). The TOF_{ov} results suggest that CeO_2 (S) has a much better toluene oxidation performance than other catalysts due to plentiful surface oxygen vacancies on it.

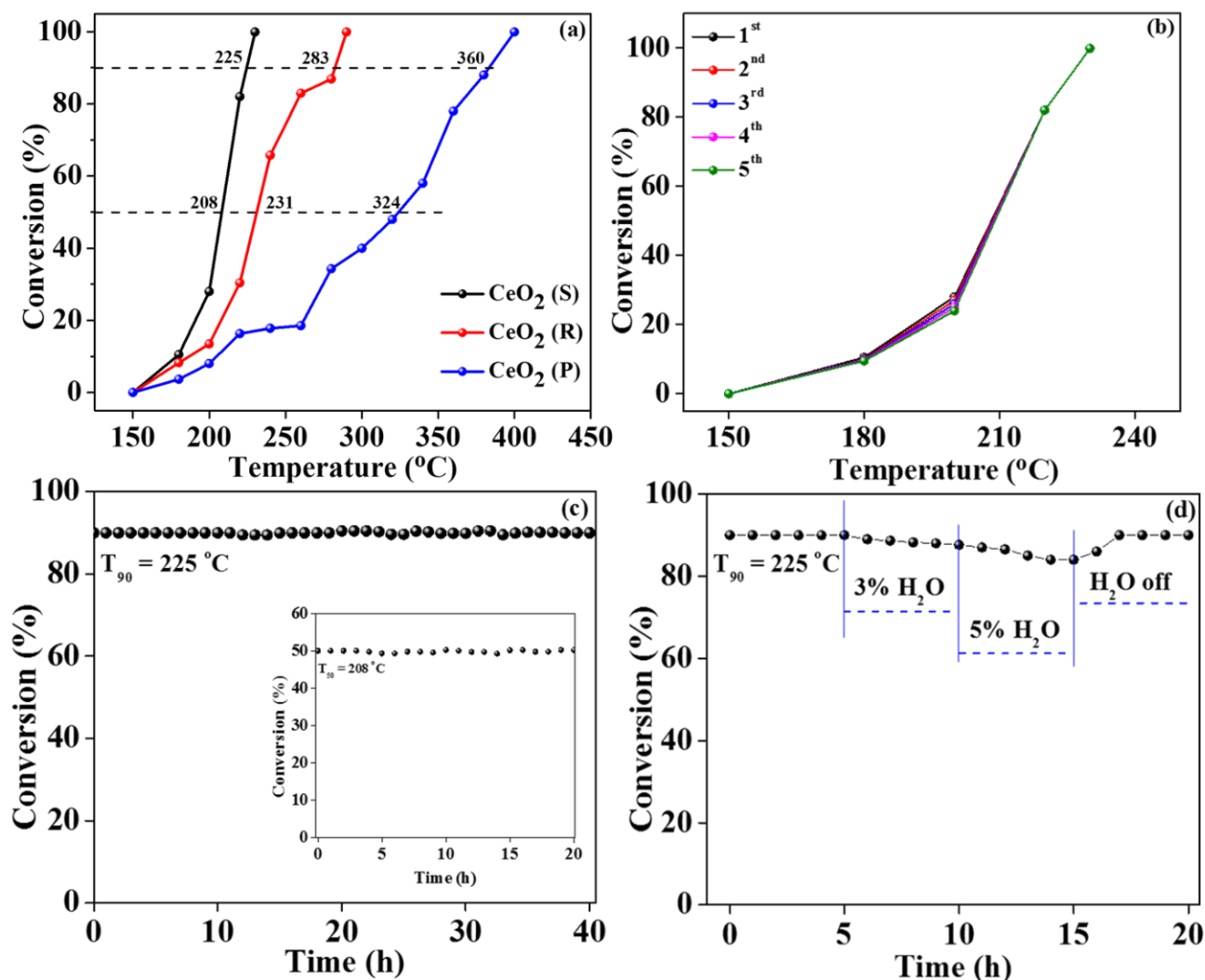


Figure 6. Catalytic oxidation activity of toluene (a) over CeO_2 (S), CeO_2 (R), and CeO_2 (P); catalytic activity for five consecutive cycles (b); catalytic activity stability as a function of time (c) and resistance to water (d) over CeO_2 (S).

Table 2. The catalytic activity, reaction rate, TOF_{ov} at 190 °C and E_a of the CeO_2 (S), CeO_2 (R), and CeO_2 (P).

Samples	T_{50} (°C)	T_{90} (°C)	Reaction Rate ($\times 10^{-2}$) ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{s}^{-1}$) (190 °C)	TOF_{ov} ($\times 10^{-4} \text{ s}^{-1}$) (190 °C)	E_a ($\text{kJ}\cdot\text{mol}^{-1}$)
CeO_2 (S)	208	225	14.37	4.8	67.4
CeO_2 (R)	231	283	7.36	2.7	85.8
CeO_2 (P)	324	360	4.26	1.4	103.2

The CeO_2 catalysts' apparent activation energy was also estimated by using Equation (4) and displayed in Figure 8. The E_a value is 67.4, 85.8 and 103.2 $\text{kJ}\cdot\text{mol}^{-1}$ over CeO_2 (S), CeO_2 (R), and CeO_2 (P), respectively. The difference in E_a values is probably because of different active surface oxygen species content, and a lower value of E_a corresponds to better catalytic activity [13,26]. The aforementioned results suggest that catalytic oxidation of toluene takes place more quickly on CeO_2 (S) than on CeO_2 (R) and CeO_2 (P). Finally, the

CeO₂ (S) catalytic oxidation activity was also compared with different morphology catalysts presented in the previous literature [8,13–15,29] (Table 3), and it can be deduced that CeO₂ (S) shuttle morphology catalysts exhibited much better catalytic oxidation activity than the previously reported different morphology catalysts.

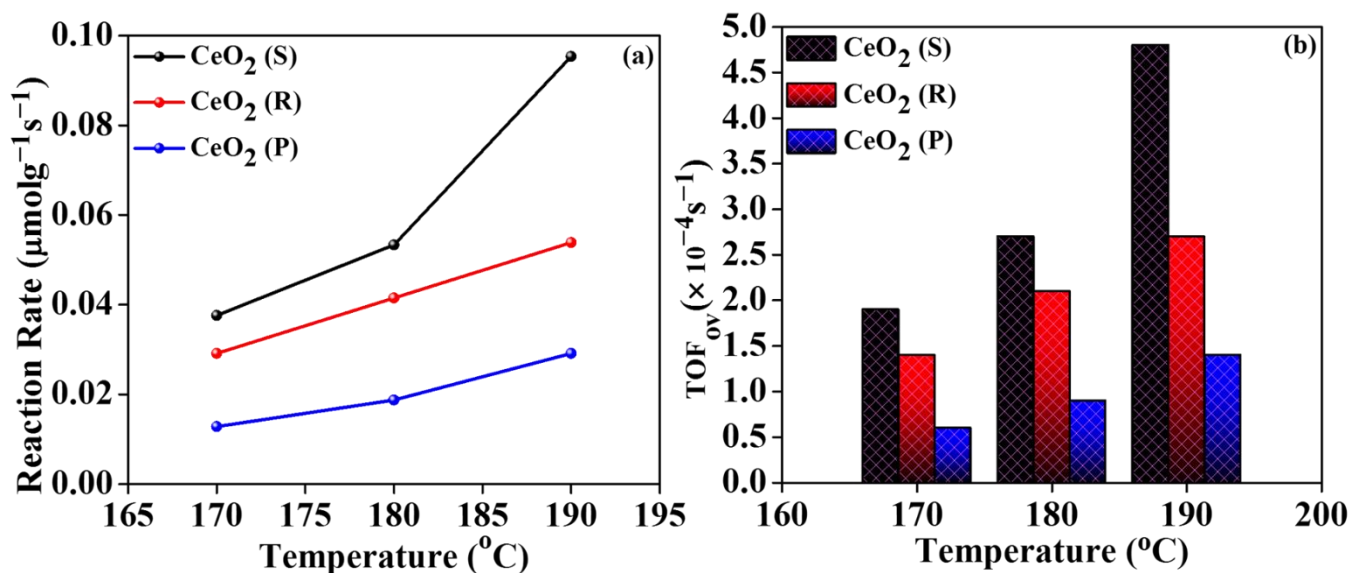


Figure 7. Reaction rate (a) and TOF_{ox} (b) over CeO₂ (S) at 170, 180, and 190 °C.

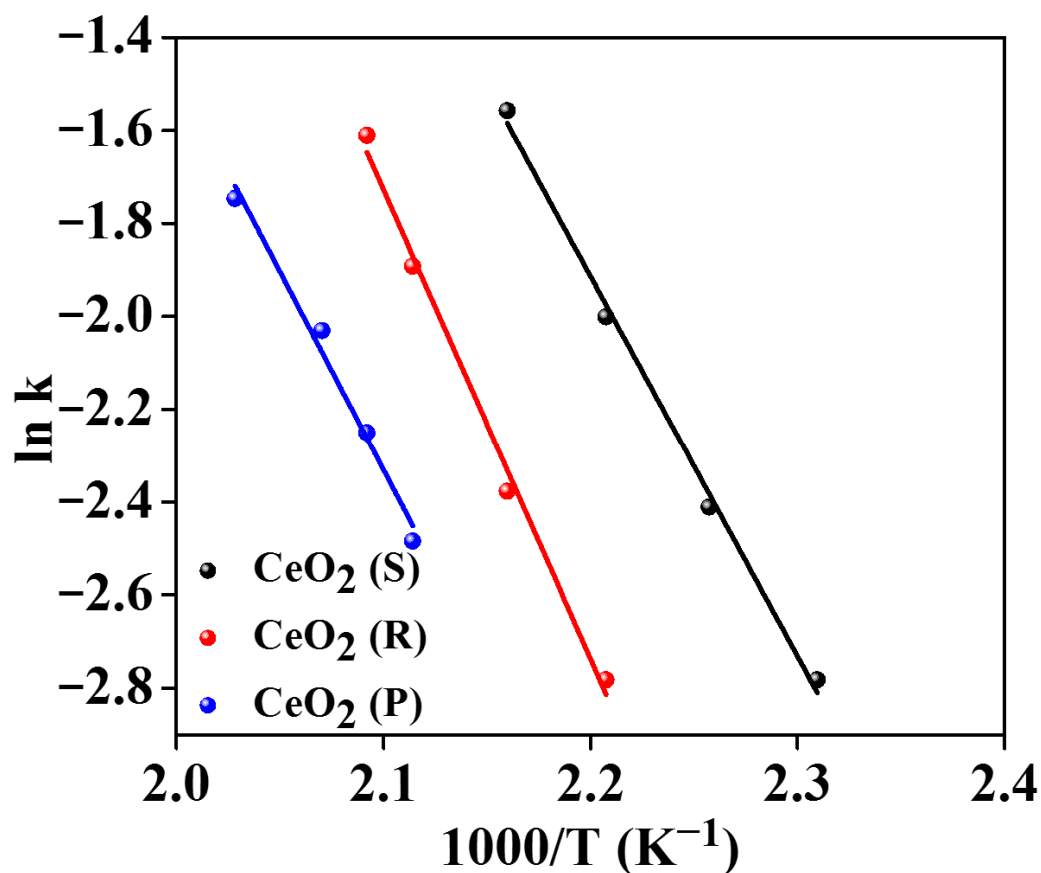


Figure 8. Arrhenius plot for toluene oxidation over CeO₂ (S), CeO₂ (R), and CeO₂ (P).

Table 3. Catalytic oxidation of toluene over different morphologies catalyst.

Catalyst	Morphology	Toluene Concentration (ppm)	WHSV mL·g ⁻¹ ·h ⁻¹	T _{90%}	Ref.
CeO ₂	Nanotubes	100	60,000	255	8
CeO ₂	Wire in nanotubes	100	60,000	345	8
CeO ₂	Nanocubes	1000	48,000	296	13
CeO ₂	Non-hierarchical Microspheres	1000	60,000	240	14
CeO ₂	Nanorods	1000	20,000	300	15
Co ₃ O ₄	Hydrangea-like microsphere	500	60,000	248	29
Co ₃ O ₄	Pompon microsphere	500	60,000	298	29
Co ₃ O ₄	Spiky microspheres	500	60,000	269	29
CeO ₂	Shuttle	1000	40,000	225	This work

2.6. Influences of Different Morphologies CeO₂ Catalysts on Oxidation Activity

The images of SEM reveal the successful formation of CeO₂ with distinct morphologies for CeO₂ (S), CeO₂ (R), and CeO₂ (P) catalysts, and they demonstrate different activity for toluene oxidation. Between them, the CeO₂ (S) catalysts display outstanding activity, which is owing to its special morphology, higher surface area and numerous oxygen vacancies, verified by the results of different characterizations. The CeO₂ (S) BET surface area (116 m²·g⁻¹) is higher than CeO₂ (R) (79 m²·g⁻¹) and CeO₂ (P) (60 m²·g⁻¹). H₂-TPR, Raman spectra and O₂-TPD suggest that CeO₂ (S) has more oxygen vacancies than CeO₂ (R) and CeO₂ (P), and the XPS results also express the finding that CeO₂ (S) has greater surface adsorbed oxygen species and surface Ce³⁺ species than CeO₂ (R) and CeO₂ (P). This is in favor of toluene catalytic oxidation. Hence, it might be deduced that the CeO₂ (S) catalyst displays excellent toluene oxidation activity as compared to CeO₂ (R) and CeO₂ (P) because of the higher surface area and plentiful surface oxygen vacancies. The CeO₂ (S)'s larger surface area and surface oxygen vacancy concentration can supply more surface active oxygen species to react with adsorbed toluene molecules, which in turn results in a higher reaction rate of toluene oxidation [31,32]. In short, different morphologies can form special surface properties, resulting in optimum catalytic oxidation activity.

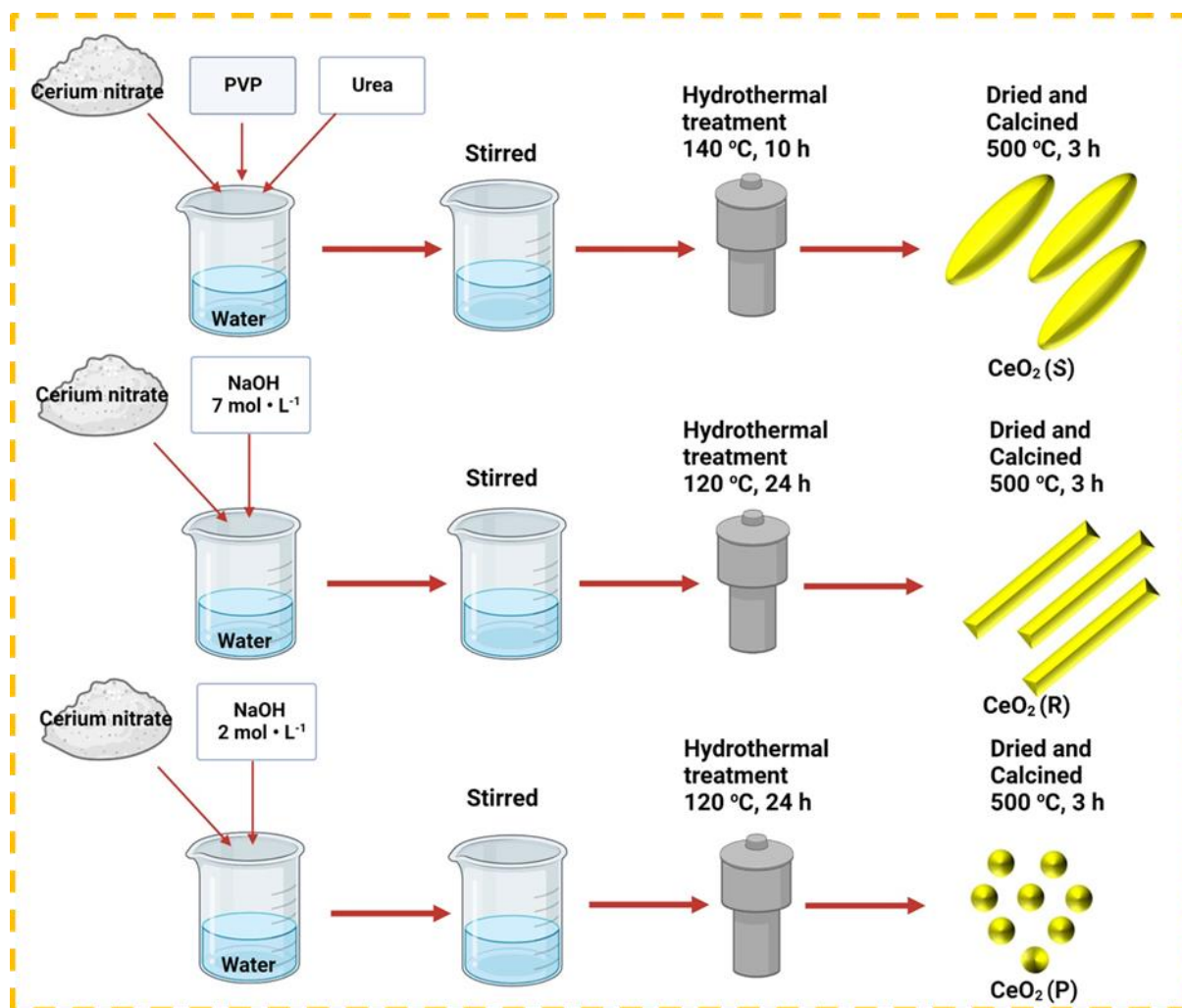
3. Experimental

3.1. Chemicals

CH₄N₂O (Tianjin Keqi Chemical Reagent Co. Ltd., Tianjin, China), Ce(NO₃)₃·6H₂O (Aladdin Industrial Corporation, Shanghai, China), NaOH, and PVP (M.W. = 30,000) (Guangdong Candlelight New Energy Technology Co., Ltd., Dongguan, China) were of high quality and used without any further treatment.

3.2. Preparation of Catalysts

The CeO₂ catalysts with shuttle, nanorods, and nanoparticle morphologies were hydrothermally synthesized. For shuttle CeO₂ (CeO₂ (S)): Ce (NO₃)₃·6H₂O (2 mmol), CH₄N₂O (15 mmol), and PVP (0.25 g) were poured in 20 mL H₂O to get a homogenous solution. In an autoclave (stainless steel), the homogenous solution was heat-treated at 140 °C for 10 h. Afterward, the product was cooled down and rinsed with distilled water and ethanol numerous times, and dehydrated at 80 °C all night. To prepare CeO₂ nanorods (CeO₂ (R)): Ce (NO₃)₃·6H₂O (10 mmol) was dispersed in distilled water (20 mL) under constant stirring. During stirring, 30 mL of 7 mol·L⁻¹ NaOH was poured into it and stirred for another half an hour. The solution was then heated at 120 °C in a stainless-steel autoclave for 24 h. Following the autoclave action, the sample was washed out and dried overnight at 80 °C. CeO₂ nanoparticles (CeO₂ (P)) were prepared in the same way as CeO₂ (R) but with a 2 mol·L⁻¹ concentration of NaOH. Finally, three distinct morphology samples were calcined for 3 h at 500 °C (1 °C·min⁻¹). The synthetic procedure scheme of the three distinct morphology catalysts is demonstrated in Scheme 1.



Scheme 1. Schematic representation of synthetic procedure of CeO₂ (S), CeO₂ (R) and CeO₂ (P).

3.3. Characterization

The surface morphology of CeO₂ catalysts was examined through SEM via JSM5910, (JEOL, Tokyo, Japan) and TEM through JEM-2100 (JEOL, Tokyo, Japan). The BET surface area was recorded by micromeritics ASAP 2020 plus 1.03 apparatus. The XRD patterns were obtained through JDX-3532 (JEOL, Japan). The Raman spectra were attained by using a Raman spectrometer (RM-2000). The chemical states were determined by XPS (Escalab 250 Xi). The reduction ability of catalysts was investigated with H₂-TPR, which was operated in a tubular reactor connected with a micromeritics Autochem 2720 chemisorption analyzer. Before measurement, in an Ar environment (30 mL·min⁻¹) the sample (100 mg) was preheated for 1 h at 300 °C. The samples were then reduced through 10% H₂/Ar (30 mL·min⁻¹) from 30–850 °C (10 °C·min⁻¹) and continuously measured by TCD (thermal conductivity detector). O₂-TPD was run in a self-build apparatus by preheating 50 mg of samples for 30 min at 300 °C in pure He gas to remove any moisture. After the moisture removal, the samples were cooled down to 30 °C under pure He gas and then subjected to O₂ for 1 h at 30 °C. The weakly adsorbed O₂ was separated by passing pure He gas, and the samples were heated from 30 °C to 700 °C (10 °C·min⁻¹) in pure He gas.

3.4. Catalytic Oxidation Activity

The catalytic oxidation of toluene was executed in a fixed-bed tube reactor attached to a gas chromatograph (FULI 9790II) coupled with an FID (flame ionization detector). The reactant mixture volumetric composition was 1000 ppm C₇H₈, N₂ (balance gas) and

20% O₂. The total gas flow rate was 100 mL·min^{−1}, corresponding to a weight hourly space velocity of 40,000 mL·g^{−1}·h^{−1} with 0.150 g catalyst. For the water vapor resistance test, 3 vol% and 5 vol% H₂O were added with the help of a water saturator in the feed. The toluene conversion (%) was calculated using Equation (1):

$$\text{Toluene conversion} = \frac{(\text{Toluene})_{in} - (\text{Toluene})_{out}}{(\text{Toluene})_{in}} \times 100\% \quad (1)$$

where, $(\text{Toluene})_{out}$ and $(\text{Toluene})_{in}$ denote the outlet and inlet concentration of toluene, respectively.

The reaction rate, r (μmol·g^{−1} s^{−1}) of the toluene conversion was assessed using Equation (2):

$$r = \frac{X_{\text{toluene}} \times V_g \times C_f}{V_m \times m_{\text{cat}}} \quad (2)$$

where X_{toluene} represents the toluene conversion (%), V_g is the gas velocity (mL·min^{−1}), C_f represents the concentration (ppm) of toluene, V_m represents the gas molar volume (22.4 L·mol^{−1}) and m_{cat} represents the catalyst mass (g), respectively.

The turnover frequency from the oxygen vacancy concentration, TOF_{ov} (s^{−1}), was calculated by using Equation (3) [14]:

$$\text{TOF}_{ov} = \frac{X_{\text{toluene}} \times C_f \times V}{\frac{m_{\text{cat}}}{M_{\text{CeO}_2}} \times (A_{600}/A_{461})} \quad (3)$$

where V denotes the toluene flow rate (mL·min^{−1}), M_{CeO_2} denotes CeO₂ molecular mass (g·mol^{−1}), A_{600}/A_{461} denotes the integral peak areas of Raman at their respective wavenumbers that were applied to evaluate the concentration of oxygen vacancies.

The apparent activation energy (E_a , kJ·mol^{−1}) was measured by using the Arrhenius Equation (4) at lower toluene conversions (less than 20%):

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (4)$$

where k represents the rate constant (mol·s^{−1}), R denotes the universal constant of gas (J·mol^{−1}·K^{−1}) and T is the temperature of the reactor (K).

4. Conclusions

In brief, CeO₂ catalysts with three distinct morphologies (CeO₂ (S), CeO₂ (R), and CeO₂ (P)) were successfully prepared through a hydrothermal approach. The as-synthesized CeO₂ (S) catalyst shows better catalytic oxidation activity than CeO₂ (R) and CeO₂ (P) catalysts, with 50% and 90% conversion at the lowest temperatures of 208 and 225 °C, correspondingly. Significantly, the optimal activity of the CeO₂ (S) catalyst can be assigned to its shuttle morphology, which has a greater surface area and many surface oxygen vacancies, resulting in better oxidation property and additional surface active oxygen species. The CeO₂ (S) catalyst also shows outstanding long-time stability, recyclability, and water resistance capability. Therefore, the CeO₂ catalyst with shuttle morphology appears as a capable catalyst in the effective control of air pollution. Furthermore, this field can be further prolonged by modifying the structural characteristics of the CeO₂ catalyst to make it more effective for VOCs oxidation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12091034/s1>. Figure S1. HRTEM images of nanorod segment of CeO₂ (S) (a and b). Figure S2. HRTEM images of CeO₂ (R) (a) and CeO₂ (P) (b).

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