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Article

Revealing the unexpected promotion effect of EuO_x on Pt/CeO_2 catalysts for catalytic combustion of toluene

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ABSTRACT

$\text{Pt}/\text{Eu}_2\text{O}_3\text{-CeO}_2$ materials with different Eu concentrations were prepared and applied to toluene destruction, and the remarkable promotion impact of EuO_x on Pt/CeO_2 can be observed. The characterization results reveal that the presence of EuO_x significantly enhances the redox property, lattice O concentration, and Ce^{3+} ratio of the Pt/CeO_2 material, which facilitates the dispersion and activity of Pt active sites and thus accelerates the decomposition process of toluene. Among all catalysts, a sample with an Eu content of 2.5 at.% ($\text{Pt}/\text{EC-2.5}$) possesses the best catalytic activity with 0.09 vol% of toluene completely destructed at 200 °C under a relatively high GHSV of 50000 h^{-1} . The possible reaction pathway and mechanism of toluene combustion over $\text{Pt}/\text{Eu}_2\text{O}_3\text{-CeO}_2$ samples are presented according to *in-situ* DRIFTS, which confirms that the toluene oxidation process obeys the Mars-van Krevelen mechanism with aldehydes and ketones as primary organic intermediates.

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1. Introduction

Volatile organic compounds (VOCs) are vital precursors of photochemical smog and ozone, which are great threats to the environment and human health owing to their toxic, carcinogenic, mutagenic, and teratogenic nature [1,2]. Ketones, alcohols, aldehydes, and aromatic compounds are the most common VOCs [3]. Toluene, a typical VOC used as an industrial feedstock and solvent, has been widely studied by researchers in recent years [4–6]. Complete catalytic oxidation is a promising way to dispose VOCs, especially with low concentration (< 0.5 vol%) [7,8]. The development of highly efficient catalysts

for abatement of VOCs at low temperature continues to attract considerable attention. Generally, there are two major types of catalysts developed for VOC oxidation: supported noble metal catalysts and transition metal oxides [9,10]. Among them, noble metal-based catalysts are preferred because of their high specific activity, resistance to deactivation, and ability to regenerate [11].

Pt-based catalysts are widely used in catalytic destruction of VOCs. Previous works reveal that the support nature can affect metal dispersion, O species mobility, metal-support interaction, and VOC molecule adsorption of Pt-based catalysts, which play crucial roles in their catalytic performance [1,11,12]. For

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Pt-based materials, a large number of supports, such as silica, zeolite, γ -Al₂O₃, carbon, and metal oxides, were studied [5,9,11–13]. Cerium oxide, which acts as a catalytic center for a series of oxidation reactions, is usually adopted as a support for noble metals because of its exceptional properties including excellent O storage capacity and high thermal stability [14,15]. For instance, Ye and co-workers [16] demonstrated the impact of the Pt particle size on the catalytic oxidation of toluene over a Pt/CeO₂ material. They found that a Pt/CeO₂ material with a Pt size of 1.8 nm has the highest toluene destruction activity due to the strong interactions between Pt and CeO₂. Zhao et al. [17] verified that the partial confinement of Pt nanoparticles in meso-channels of micro-sized mesoporous CeO₂ leads to a significant enhancement in the activity of surface lattice O around the interface between Pt nanoparticles and CeO₂, and thus tremendously increasing the catalytic activity for benzene conversion. Eu is one of the most reactive rare earth elements. It has been applied to VOC elimination in recent years [18,19]. Ji et al. [20] proposed that 3DOM Eu_{0.6}Sr_{0.4}FeO₃ possessed superior catalytic activity in toluene combustion attributing to the synergistic effect of these metal oxides. Meanwhile, Parvulescu and co-workers [18] reported a case study of the cooperative effects of the rare earth and transition metal elements (EuFeO₃ perovskite-type oxides) in the total catalytic oxidation of aromatic hydrocarbons. They concluded that the introduction of Eu species promotes the formation of O vacancies in the proximity of Eu cations during the reaction. However, EuO_x-CeO₂ has never been applied as a Pt-based catalyst support in oxidation reactions. As such, it is of great interest to investigate and reveal the synergistic effect of EuO_x and CeO₂ on supported Pt catalysts in VOC oxidation, which could provide additional alternatives in design of efficient catalysts.

In this study, we synthesized a series of Pt/Eu₂O₃-CeO₂ (defined as Pt/EC-*x*) catalysts with different Eu contents and used them for toluene oxidation. The results show that the activity of the Pt/Eu₂O₃-CeO₂ catalysts is better than that of the traditional Pt/CeO₂ materials. Pt/EC-2.5 (Eu = 2.5 at.%) exhibits the highest decomposition activity with toluene totally eliminated at 200 °C. The synergistic effect between EuO_x and CeO₂ obviously enhances the specific surface area, redox property, lattice O concentration, and Ce³⁺ ratio of the Pt/CeO₂ material, which are beneficial for the superb catalytic performance of the Pt/Eu₂O₃-CeO₂ materials.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of Eu₂O₃-CeO₂ supports

Eu-doped CeO₂ materials were successfully prepared using a surfactant template protocol with Ce(NO₃)₃·6H₂O (99.9%) and CH₃(CH₂)₁₁SO₄Na (99.0%) as a precursor and a template, respectively. Typically, 7.844 g (Ce(NO₃)₃·6H₂O) was dissolved in 40 mL deionized water and kept stirring for 2 h. Following this, a 100 mL Eu(NO₃)₃·6H₂O aqueous solution with different Eu contents (0, 2.5, 5, and 10 at.%) was dropwise added and stirred for 0.5 h. Subsequently, 100 mL of a NaOH (1.7 g)

aqueous solution was added to the mixture. The resulting precipitate was stirred at room temperature for 24 h and then aged at 90 °C for 72 h. Then, the obtained materials were washed thoroughly using deionized water, dried for 3 h at 70 °C, and calcined at 400 °C for 4 h (heating rate = 3 °C min⁻¹). The obtained materials with different Eu contents were denoted as EC-0, EC-2.5, EC-5, and EC-10, respectively. In addition, traditional CeO₂ was prepared via a sol-gel method according to the reported procedures [21].

2.1.2. Synthesis of Pt/Eu₂O₃-CeO₂ and Pt/CeO₂ catalysts

Pt/Eu₂O₃-CeO₂ and Pt/CeO₂ materials (nominal Pt weight = 0.5 wt%) were synthesized by dispersing Eu₂O₃-CeO₂ and CeO₂ into an H₂PtCl₆·6H₂O solution under stirring. After being stirred for 20 min, the mixed solution was added into a rotary evaporator and evaporated at 50 °C under rotation. After that, the resulting powder was continuously dried at 80 °C for 12 h and calcined at 400 °C for 2 h. The obtained material was reduced by H₂ at 300 °C for 1 h to obtain Pt/CeO₂, Pt/EC-0, Pt/EC-2.5, Pt/EC-5, and Pt/EC-10 catalysts.

2.2. Catalyst characterization

Field emission scanning electron microscopy (FE-SEM) images were recorded using a JEOL 7800F (Japan) microscope. High-resolution transmission electron microscopy (HR-TEM) images were collected on a G2F30 microscope (FEL, America) operating at an acceleration voltage of 300 kV. XRD measurements were performed using a powder diffractometer (PANalytical, Netherlands) with Cu-K α radiation. X-ray photoelectron spectroscopy (XPS) experiments were carried out by means of an AXIS ULTRABLD instrument (Kratos, UK) with Mg-K α radiation ($h\nu$ = 1253.6 eV). N₂ sorption isotherms were measured at -196 °C on a Builder SSA-6000 apparatus. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was derived from the desorption branch of the N₂ isotherms using the Barrett-Joyner-Halenda (BJH) method. The actual Pt content of the samples was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on ICPE-9000 (SHIMADZU, Japan). H₂-TPR, O₂-TPD, and H and O titration (HOT) were performed on PCA-1200 equipped with a TCD. *In-situ* DRIFTS spectra of the toluene oxidation were recorded with Bruker Tensor 37 with an MCT detector in the range of 600–4000 cm⁻¹, with a resolution of 4 cm⁻¹ and 64 acquisition scans. The detailed methods of each technique are described in Supporting Information.

2.3. Catalytic activity

The catalytic oxidation of toluene was performed in a continuous-flow fixed-bed reactor (inside diameter = 6 mm) at ambient pressure. A 0.40 g catalyst (40–60 mesh) was placed into the tube reactor in each test. A total of 0.09 vol% of toluene was generated by an N₂ bubbler in a thermostatic bath at 30 °C and mixed with air (total flow rate = 200 mL min⁻¹, GHSV = 50000 h⁻¹). The concentrations of toluene, CO, and CO₂ were

Fig. 1. XRD patterns of the prepared samples: (a) Pt/CeO₂, (b) Pt/EC-0, (c) Pt/EC-2.5, (d) Pt/EC-5, and (e) Pt/EC-10.

measured using an on-line gas chromatograph (GC-9890B) equipped with a flame ionization detector and an HT-Wax column in 30 m × 0.32 mm (inside diameter) × 0.5 μm. The toluene conversion (X_{toluene}) was calculated as Eq. (1),

$$X_{\text{toluene}}(\%) = ([\text{toluene}]_{\text{in}} - [\text{toluene}]_{\text{out}}) / [\text{toluene}]_{\text{in}} \times 100\% \quad (1)$$

where $[\text{toluene}]_{\text{in}}$ and $[\text{toluene}]_{\text{out}}$ are the concentrations of toluene in inlet and outlet gas, respectively.

The reaction rate (r_{toluene} , mmol g⁻¹ s⁻¹) was calculated as Eq. (2),

$$r_{\text{toluene}} = X_{\text{toluene}} \cdot V_{\text{toluene}} / W_{\text{cat}} \quad (2)$$

where W_{cat} is the catalyst weight (g) and V_{toluene} is the toluene gas flow rate (mol s⁻¹).

The turnover frequency based on Pt nanoparticles (TOF_{Pt} , s⁻¹) was calculated as Eq. (3),

$$\text{TOF}_{\text{Pt}} = X_{\text{toluene}} \cdot V_{\text{toluene}} \cdot N_A / (W_{\text{cat}} \cdot w\%_{\text{Pt}} \cdot D_{\text{Pt}}) \quad (3)$$

where N_A is the Avogadro constant and D_{Pt} represents the dispersion of Pt nanoparticles on catalysts (%).

3. Results and discussion

3.1. Structural and textural properties

Fig. 1 shows the XRD patterns of the Pt/CeO₂ and Pt/EC-*x* catalysts. It can be observed that all samples possess diffraction peaks at 2θ of 28.5°, 33.1°, 47.4°, 56.3°, 59.1°, 69.5°, 76.7°, and 79.1°, respectively corresponding to the (111), (200), (220), (311), (222), (400), (331), and (420) facets of CeO₂ [22], indicating the presence of the cubic phase of fluorite oxide-type CeO₂ (JCPDS PDF #34-0394) [23]. No diffraction peaks corresponding to the EuO_x crystalline phases can be found over all Pt/EC-*x* catalysts, which is assigned to sizable dispersion of EuO_x with too small particle size over metal oxides or the incorporation of Eu in the CeO₂ lattice [24]. The characteristic peaks of Pt (the shoulder peak at 39.8°) can hardly be observed in all catalysts mainly owing to the low content, small particle size, and high dispersion of Pt sites [12]. Importantly, the intensity of diffraction peaks becomes weaker after the incorporation of Eu species, suggesting that the crystallite size of Pt/EC-*x* declines to some extent as compared to that of CeO₂, and the addition of Eu species weakens the Ce–O bond [22].

The textural properties of the prepared samples were investigated by low-temperature N₂ sorption, as shown in Fig. 2. Pt/CeO₂ has a type II and IV hybrid isotherm with a distinct H3 type hysteresis loop at $P/P_0 = 0.45$ –1.0 [12]. However, the N₂ sorption isotherm of the Pt/EC-*x* samples indicates the existence of the framework-confined mesopores [25]. The pore size distributions calculated for all samples are mainly in the range of 3–4 nm, confirming the presence of abundant mesopores. The average pore diameter of the Pt/EC-*x* samples declines with the increase in the Eu content, which is probably ascribed to the partial blockage of pore channels after the incorporation of Eu [26]. The structural parameters of all samples are listed in Table 1. All Pt/EC-*x* catalysts possess higher A_{BET} , V_{pore} , and d_p than traditional Pt/CeO₂, which is beneficial for toluene decomposition. Additionally, all A_{BET} , V_{pore} , and d_p became larger after the activity test because of carbon deposition during the oxidation reaction [27].

The morphology of the Pt/EC-*x* catalysts was characterized by FE-SEM. As depicted in Figs. 3a–d, the prepared Pt/EC-*x* samples with a particle size of 1–3 μm are bulk. It can be con-

Fig. 2. (A) N₂ adsorption-desorption isotherms and (B) pore size distribution of all samples.

Table 1

Textural properties of the synthesized catalysts.

Sample	Pt content ^a (wt.%)	Dispersion ^b (%)	A_{BET} ^c ($\text{m}^2 \text{g}^{-1}$)	V_{pore} ^d ($\text{cm}^3 \text{g}^{-1}$)	d_{pore} ^e (nm)
Pt/CeO ₂	0.55	16.35	17.1 (20.8) ^f	0.08 (0.06)	19.08 (10.68)
Pt/EC-0	0.61	27.86	130.1 (129.4)	0.13 (0.18)	3.92 (5.66)
Pt/EC-2.5	0.65	32.58	133.2 (143.8)	0.12 (0.19)	3.54 (5.44)
Pt/EC-5	0.52	18.44	135.3 (148.3)	0.10 (0.14)	3.02 (3.70)
Pt/EC-10	0.63	27.69	133.7 (129.7)	0.09 (0.15)	2.94 (4.50)

^a Nominal Pt content detected by ICP-OES.^b Dispersion of Pt estimated by HOT.^c Specific surface area obtained at $P/P_0 = 0.05$ – 0.30 .^d Total pore volume estimated at $P/P_0 = 0.99$.^e BJH pore diameter calculated from the desorption branch.^f Parameters of the used materials are listed in brackets.

firm that the morphology of the bulk samples was changed after the Eu doping. The particle aggregation in the Pt/EC-*x* samples can be confirmed by increasing the content of Eu. The detailed microstructure of the Pt/EC-0 and Pt/EC-2.5 materials was further examined by HR-TEM, as shown in Figs. 4a,b. It can be found that Pt nanoparticles are homogeneously dispersed over the Pt/CeO₂ and Pt/EC-2.5 catalysts. The fringes of the CeO₂, Eu, and Pt crystal lattices are clearly observed corresponding to the (111), (220), (521), and (200) planes with distances of 0.31, 0.27, 0.19, and 0.19 nm, respectively. According to the literature, CeO₂ with exposed (111) plane exhibits higher activity for supported Pt catalysts [26]. Meanwhile, the confinement of Pt, CeO₂, and Eu species is unclear, corresponding to the intense interaction between these species, which is attributed to the weakening of the Ce–O bond. In addition, the mapping elemental distributions of the Pt/EC-2.5 sample are shown in Figs. 4c–f and Fig. S1 (in Supporting Information). The images show that all elements in the prepared catalyst are distributed uniformly, which indicates the homogeneous distribution of Pt, Ce, and Eu over the prepared catalyst. In particular, the dispersion of Pt active sites was determined by the HOT method and listed in Table 1. The Pt/EC-2.5 catalyst possesses the highest dispersion (32.58%) among all these samples, which is seen to be beneficial for toluene combustion over catalysts.

3.2. Redox property and surface status

The reducibility of the synthesized catalysts was evaluated by a temperature-programmed reduction experiment, as shown in Fig. 5A. The first small reduction peak at 93–119 °C is ascribed to the transfer from PtO to Pt [26]. However, the H₂ consumption amount is much higher than that needed for the reduction of PtO_x at 87 °C, which indicates that most of H is consumed by Eu₂O₃–CeO₂ contacting with Pt owing to the H spillover from Pt species to CeO₂ [28]. In general, lattice O of CeO₂ (without any additives) is often reduced at around 500 °C, which is shifted to lower temperature when referring to the binary CeEuO_x oxides. In this H₂-TPR profiles, the peak above 700 °C is ascribed to the bulk O reduction and the peak centered at 350–600 °C can be attributed to Ce⁴⁺ to Ce⁰ [24]. Compared with Pt/CeO₂, the peak of the surface lattice O reduction moves to the higher temperature region for the Pt/EC-*x* materials, indicating that the introduction of Eu changes lattice O of CeO₂. Table S1 summarizes the results of the quantitative analysis of the H₂-TPR profiles of the samples. The lowest reduction temperature of the Pt/EC-2.5 catalyst confirms its superior redox ability, in line with the catalytic performance of the toluene combustion. Obviously, the total H₂ consumption (0.84 mmol g^{−1}) of Pt/EC-2.5 is much higher than that of other samples (0.17–0.59 mmol g^{−1}), indicating the abundant amount of

Fig. 3. FE-SEM images of (a) Pt/EC-0, (b) Pt/EC-2.5, (c) Pt/EC-5, and (d) Pt/EC-10 samples.

Fig. 4. HR-TEM images of (a) Pt/EC-0 and (b) Pt/EC-2.5 samples; (c–f) EDS-mapping images of Pt/EC-2.5.

Fig. 5. (A) H₂-TPR profiles and (B) initial H₂ consumption rate as a function of inverse temperature of (a) Pt/CeO₂, (b) Pt/EC-0, (c) Pt/EC-2.5, (d) Pt/EC-5, and (e) Pt/EC-10 samples.

surface O species over the Pt/EC-2.5 catalyst [26].

In order to better evaluate the low-temperature reducibility of the samples, we calculated the initial H₂ consumption rate as a function of the inverse temperature of the synthesized materials. Figure 5B shows that the initial H₂ consumption rates of the prepared samples decrease in the sequence of Pt/EC-10 > Pt/EC-5 > Pt/EC-2.5 > Pt/EC-0 > Pt/CeO₂, indicating that the introduction of Eu increases the reducibility of the materials. The H₂-TPR results suggest that Eu obviously enhances the mobility of surface lattice O species of CeO₂, which is attributed to the synergetic effect between EuO_x and CeO₂ in binary oxides by weakening the Ce–O–Eu chemical bonds [22]. The sufficient amount of surface lattice O species with high mobility is essential for toluene combustion, and the synergetic effect probably plays a key role in this process acceleration [29].

The surface chemical state of the prepared materials was studied by X-ray photoelectron spectroscopy. Fig. 6 displays the spectra of Pt 4f, Ce 3d, Eu 3d, and O 1s regions of the Pt/EC-*x* samples, and the full spectra are shown in Fig. S2. As shown in Fig. 6A, considering the O 1s XPS spectra, the shoulder peaks at approximately 533–534, 531–532, and 529–530 eV are ascribed to O species associated with adsorbed O species (O_{ads}), surface O (O_{surf}), and lattice O (O_{latt}), respectively [25,30]. Surface and lattice O is assigned to defect oxide or surface O ions with low coordination situation and weakly bonded O species [31]. The percentages of O_{latt}/(O_{latt} + O_{surf}) are listed in Table S2. The calculated percentage of O_{latt} in Pt/EC-2.5 (43.8%) is much higher than that in Pt/CeO₂ (37.1%), Pt/EC-0 (34.3%), Pt/EC-5 (33.9%), and Pt/EC-10 (35.4%) samples, indicating that the doping of Eu into the framework of CeO_x may lead to activity variations of the materials toward toluene decomposition [24]. The Ce 3d spectra of the prepared samples are listed in Fig. 6B, and two types of cerium species (Ce³⁺ and Ce⁴⁺) can be observed. The “v” and “u” peaks correspond to the 3d_{5/2} and 3d_{3/2} states, respectively [32]. According to previous reports, four peaks v”, v”, u”, and u” are indicators of the existence of Ce⁴⁺; meanwhile, other peaks v, v’, u, and u’ can be assigned to Ce³⁺, which is associated with the presence of abundant O vacancies

[32,33]. The relative content of Ce³⁺ can be determined by $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+}) \times 100\%$, and the results in Table S2 reveal that there is no significant difference in the Ce³⁺ percentages among samples with different Eu concentrations. Besides, the contents of Ce³⁺ in all Pt/EC-*x* catalysts (37.2%–41.8%) are higher than those of the Pt/CeO₂ (31.1%) sample, which indicates that the surfactant template method is incline to produce sufficient O vacancies compared to the sol-gel approach. Fig. 6C presents the Pt 4f XPS spectra of the Pt/EC-*x* samples, and the peaks centered at 72.7 and 75.6–76.7 eV are assigned to Pt⁰ and Pt²⁺, respectively [12,16]. The calculated ratio of Pt⁰/(Pt⁰ + Pt²⁺) is listed in Table S2. The higher ratio of Pt⁰ active sites is beneficial for toluene combustion [25]. The XPS result of Eu 3d is shown in Fig. 6D. All Eu 3d spectra of Eu-contained samples have two main peaks with binding energies of 1134.5 and 1165.1 eV ascribed to the Eu 3d_{5/2} and Eu 3d_{3/2} final states of Eu³⁺, respectively [18,19], and the signal intensity increases with the Eu content.

3.3. Catalytic performance

The catalytic performance of the toluene oxidation of the Pt/CeO₂ and Pt/EC-*x* samples was studied, and the related parameters are presented in Fig. 7 and Table 2. The Pt/CeO₂ catalyst can destruct 90% of toluene at 233 °C, which is slightly better than that of Pt/EC-0 (*T*₉₀ of 270 °C). Compared with the Pt/EC-0 sample, the Pt/EC-*x* materials exhibit much higher toluene oxidation activity (Fig. 7A), indicating that the introduction of Eu is beneficial for the performance of the Pt/EC-*x* samples during the toluene combustion. Among them, the Pt/EC-2.5 material is identified as the best catalyst, which can eliminate 90% of toluene at 188 °C, which is obviously higher than that of other materials with *T*₉₀ temperature in sequence of Pt/EC-5 (193 °C) < Pt/EC-10 (196 °C) < Pt/CeO₂ (233 °C) < Pt/EC-0 (270 °C). The reaction stability and the water vapor resistance are important parameters for estimating the activity of supported Pt catalysts. As shown in Fig. 7B, the performance of the toluene combustion of the Pt/EC-2.5 catalyst was stable

Fig. 6. XPS spectra of (a) Pt/CeO₂, (b) Pt/EC-0, (c) Pt/EC-2.5, (d) Pt/EC-5, and (e) Pt/EC-10 samples: (A) O 1s; (B) Ce 3d; (C) Pt 4f; (D) Eu 3d.

at 190 °C for 20 h with a GHSV of 50000 h⁻¹, demonstrating its excellent stability in the complete toluene decomposition. The water vapor resistance test for the toluene combustion was conducted using a typical Pt/EC-2.5 catalyst. The results are displayed in Fig. S3. A loss in the toluene combustion efficiency of approximately 15.7% was observed over the Pt/EC-2.5 catalyst when 2.5 vol% water vapor was introduced into the stream. The water vapor was found to have a negative effect on the combustion of toluene, which is likely to be due to the competitive adsorption of H₂O, toluene, and O₂ molecules on the catalyst surface. However, when the water vapor was switched off, the conversion of toluene restored to the almost original values within few minutes, which indicated that the prepared Pt/EC-2.5 catalyst possesses considerable water-resistant ability. Meanwhile, the performance of the toluene combustion of the Pt/EC-2.5 sample is also well-maintained in the cases of heating and cooling circles (Fig. 7C). The good stability provides the possibility of use of Pt/EC-*x* materials in practical elimination of VOCs. The *E_a* of the toluene decomposition calculated using the Arrhenius plots is introduced to evaluate the catalytic capacity of the prepared materials. As displayed in Fig. 7D, the activation energies increase as Pt/EC-0 (40.22 kJ mol⁻¹) < Pt/EC-2.5 (43.16 kJ mol⁻¹) < Pt/EC-10 (55.53 kJ mol⁻¹) < Pt/EC-5 (73.79 kJ mol⁻¹) < Pt/CeO₂ (74.87 kJ mol⁻¹). Lower *E_a* of the toluene oxidation over the Pt/EC-*x* catalysts

suggests their better toluene destruction activity.

The turnover frequency (Fig. 8A) and the destruction rate (Fig. 8B) are further adopted to the in-depth view the intrinsic performance of the toluene oxidation over the prepared catalysts [12]. As shown in Fig. 8A, the Pt/EC-2.5 catalyst shows a very high turnover frequency (5.52 s⁻¹) of the toluene oxidation at 160 °C, which is five times higher than that of Pt/EC-0 (1.06 s⁻¹ at 160 °C). The TOF_{Pt} of the catalysts for toluene elimination at 160 °C is ranked as Pt/EC-10 (6.01 × 10⁻² s⁻¹) > Pt/EC-2.5 (5.52 × 10⁻² s⁻¹) > Pt/EC-5 (6.01 × 10⁻² s⁻¹) > Pt/CeO₂ (4.13 × 10⁻² s⁻¹) > Pt/EC-0 (1.06 × 10⁻² s⁻¹), demonstrating that the incorporation of Eu species greatly enhances the catalytic efficiency of the Pt/CeO₂ materials in the oxidation of toluene. In addition to this, the reaction rate of the toluene oxidation of Pt/EC-2.5 (0.009 mmol g⁻¹ s⁻¹) is significantly higher than that of the Pt/EC-0 material (0.001 mmol g⁻¹ s⁻¹) at 160 °C. As shown in Figs. 8B,C and Table 2, the calculated reaction rates of the catalytic decomposition of toluene at 160 °C decrease in the sequence of Pt/EC-2.5 (0.009 mmol g⁻¹ s⁻¹) > Pt/EC-10 (0.008 mmol g⁻¹ s⁻¹) > Pt/EC-5 (0.003 mmol g⁻¹ s⁻¹) > Pt/EC-0 (0.001 mmol g⁻¹ s⁻¹), in line with the sequence at 180 °C, demonstrating an excellent activity of the Eu-contained catalysts.

3.4. Mechanism study

Fig. 7. (A) Catalytic activity, (B) reaction stability, (C) heating-cooling circle test, and (D) Arrhenius plots of the toluene catalytic combustion of the prepared catalysts.

The study of the possible formation scheme of partial oxidation products and subsequent promotion of the CO₂ yield is one of the most significant issues for environment-friendly VOC elimination [12]. As a consequence, *in-situ* DRIFTS of the toluene oxidation over the prepared catalysts was studied at different reaction temperatures to explore the destruction mechanism. For the Pt/CeO₂ catalyst (Fig. 9A), the peak at 3654 cm⁻¹ is assigned to the surface -OH group during oxidation [33,34].

Table 2

Catalytic performance of the synthesized catalysts.

Sample	T_{50}^a (°C)	T_{90}^a (°C)	$r_v \times 10^{2b}$ (mmol g ⁻¹ s ⁻¹)	E_a^c (kJ mol ⁻¹)	TOF _{Pt} ^d $\times 10^2$ (s ⁻¹)
Pt/CeO ₂	218	233	0.3	74.87	4.13
Pt/EC-0	247	270	0.1	40.22	1.06
Pt/EC-2.5	170	188	0.9	43.16	5.52
Pt/EC-5	172	193	0.3	73.79	3.71
Pt/EC-10	173	196	0.8	55.53	6.01

^a Temperatures at which the conversion of toluene is 50% and 90%.

^b Reaction rate of toluene transformed per surface area per unit time of various catalysts at 160 °C.

^c Apparent activation energy obtained from the Arrhenius plot.

^d Turnover frequency based on the dispersion of Pt obtained at 160 °C.

The bands at 1357–1395 cm⁻¹ are the symmetric vibrations of C=O species, indicative of intermediates of aldehydes or ketones [35]. Meanwhile, the observed peak at 1537 cm⁻¹ is ascribed to the vibration of -CH₃ groups [36]. However, the reaction mechanism of the toluene decomposition over Pt/EC-2.5 is slightly different, as shown in Fig. 9B. The inconspicuous peaks from 2782 cm⁻¹ to 3025 cm⁻¹ are stretching singles of C-H or C-C species in toluene or intermediates [34]. In addition, the band at 1658 cm⁻¹ is the asymmetric vibrations of C=O species [36]. The results indicate that the reaction by-products are rarely detected over the Eu-doped materials. The possible reaction pathway of the toluene combustion over Pt/EC-2.5 is proposed and shown in Scheme 1. The toluene combustion over the prepared Pt-based materials involves the Mars-van Krevelen mechanism [37,38], where toluene is primarily adsorbed over the surface of oxide support and decomposed by Pt active sites associated with lattice O, and the O vacancies are produced. After being adsorbed to this material, toluene is first decomposed to produce ketone and subsequently undergoes a similar transformation to aldehyde, a process which is again assisted by the donation of a proton from the Brönsted acid

Fig. 8. (A) Turnover frequency based on the Pt dispersion, (B) reaction rate of the toluene catalytic combustion of the prepared catalysts, and (C) comparison of the reaction rates of the active samples at 160 and 180 °C.

Fig. 9. In-situ DRIFTS spectra of the toluene oxidation of (A) Pt/CeO₂ and (B) Pt/EC-2.5 as a function of the reaction temperature in flowing toluene + N₂ + O₂ from 80 °C to 300 °C.

sites. The obtained aldehyde was totally converted into harmless H₂O and CO₂. Finally, the O vacancies were replenished by adsorbed O atoms.

4. Conclusions

A series of Pt/Eu₂O₃-CeO₂ (defined as Pt/EC-*x*) catalysts with different Eu contents were successfully fabricated and used for the toluene total decomposition. Pt/Eu₂O₃-CeO₂ materials exhibit much higher toluene elimination efficiency attributing to the promotion impact of EuO_x on Pt/CeO₂. The

Pt/EC-2.5 sample shows the best toluene destruction activity, which can completely decompose 0.09 vol.% of toluene at 200 °C under a GHSV of 50000 h⁻¹. Compared with traditional Pt/CeO₂, higher specific area, superior redox properties, abundant lattice O, and higher ratio of Ce³⁺ are demonstrated for the Pt/Eu₂O₃-CeO₂ materials, which are ascribed to the synergistic effect between EuO_x and CeO_x oxides, which facilitates the dispersion and activity of Pt active sites and thus accelerates the decomposition process of toluene.

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Scheme 1. Schematic of the mechanism of the toluene catalytic oxidation over the Pt/EC-2.5 catalyst.

Graphical Abstract

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Revealing the unexpected promotion effect of EuO_x on Pt/CeO_2 catalysts for catalytic combustion of toluene

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The presence of EuO_x species greatly enhances the redox property, lattice O concentration, and Ce^{3+} ratio of Pt/CeO_2 , and subsequently low-temperature toluene destruction is achieved.

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稀土氧化物 EuO_x 对 Pt/CeO_2 材料在甲苯催化燃烧中的显著促进机制

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摘要: 挥发性有机污染物是大气环境中一类重要的污染物质, 其污染控制问题已成为21世纪大气污染控制的优先方向之一。甲苯作为一种典型芳香烃在医药、农药、染料合成等多个化工行业中常用作有机化工原料并被排入大气环境, 对人类的生产和生活造成极大危害。由于其高致癌性, 甲苯在2017年被世界卫生组织国际癌症研究机构列为3类致癌物。在甲苯的催化燃烧降解中, 负载型铂基催化剂由于其高效的低温催化活性被学者广泛研究。 CeO_2 作为一种典型的稀土金属氧化物具有较强的储放氧能力和高温稳定性, 被视为负载型贵金属催化剂的优良载体。近期研究表明, EuO_x 具有良好的催化氧化活性, 并能促进金属氧化物表面氧缺位的形成。为了进一步研究 EuO_x 与 CeO_2 之间的协同效应对贵金属基催化剂低温催化性能的影响, 我们利用表面模板剂法合成了具有不同Eu负载量的 $\text{Pt/Eu}_2\text{O}_3\text{-CeO}_2$ 材料并应用于甲苯的深度催化氧化。研究表明, EuO_x 的加入显著提高了 Pt/CeO_2 材料的催化性能, 当Eu含量为2.5 at%时(Pt/EC-2.5)该材料拥有最佳的低温氧化活性, 可在200 °C实现对0.09%甲苯的完全降解, 在160 °C时反应速率和转化频次分别高达 $0.9 \text{ mmol g}^{-1} \text{ s}^{-1}$ 和 $5.52 \times 10^2 \text{ s}^{-1}$ 。相比于 Pt/CeO_2 催化剂, EuO_x 与 CeO_2 之间的协同作用极大提高了催化剂的氧化还原性能, 增大了材料表面晶格氧和 Ce^{3+} 的含量, 并显著提高了贵金属活性相的分散度。通过原位漫反射红外光谱在线分析了甲苯在 $\text{Pt/Eu}_2\text{O}_3\text{-CeO}_2$ 材料表面的深度降解机理。与甲苯在 Pt/CeO_2 材料表面的氧化行为相比, 甲苯在 Pt/EC-2.5 催化剂表面的降解遵循典型的Mars-van Krevelen (MvK)机理。当吸附于稀土金属氧化物载体后, 在Pt活性位点、晶格氧及表面酸性位点的联合作用下, 甲苯以酮类和醛类为主要的中间产物, 被迅速深度氧化为 H_2O 和 CO_2 。

关键词: $\text{Pt/Eu}_2\text{O}_3\text{-CeO}_2$ 材料; 协同作用; 甲苯; 催化氧化; 原位红外漫反射光谱; 反应机理

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