

Catalytic combustion of volatile aromatic compounds over CuO-CeO₂ catalyst

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Abstract—Ce_{1-x}Cu_xO₂ oxide solid solution catalysts with different Ce/Cu mole ratios were synthesized by the one-pot complex method. The prepared Ce_{1-x}Cu_xO₂ catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and H₂ temperature-programmed reduction (H₂-TPR). Their catalytic properties were also investigated by catalytic combustion of phenyl volatile organic compounds (PVOCs: benzene, toluene, xylene, and ethylbenzene) in air. XRD analysis confirmed that the CuO species can fully dissolve into the CeO₂ lattice to form CeCu oxide solid solutions. XPS and H₂-TPR results indicated that the prepared Ce_{1-x}Cu_xO₂ catalysts contain abundant reactive oxygen species and superior reducibility. Furthermore, the physicochemical properties of the prepared Ce_{1-x}Cu_xO₂ catalysts are affected by the Ce/Cu mole ratio. The CeCu₃ catalyst with Ce/Cu mole ratio of 3.0 contains abundant reactive oxygen species and exhibits superior catalytic combustion activity of PVOCs. Moreover, the ignitability of PVOCs is also affected by the respective physicochemical properties. The catalytic combustion conversions of ethylbenzene, xylene, toluene, and benzene are 99%, 98.9%, 94.3%, and 62.8% at 205, 220, 225, and 225 °C, respectively.

Keywords: Ce_{1-x}Cu_xO₂ Oxide Solid Solution, Catalyst, Phenyl VOCs, Catalytic Combustion, Reactive Oxygen Species

INTRODUCTION

With the rapid development of social economy, phenyl volatile organic compound (PVOC) emissions are increasing, thereby intensifying environment and human health hazards. PVOCs mainly include benzene, toluene, xylene, ethylbenzene, and other organic compounds, which are widely used in paints, resins, organic adhesives, leather, petrochemical, and other industrial production processes. PVOCs can be directly emitted into the atmosphere and groundwater environment in the corresponding industrial production process, which can seriously harm human health and the environment [1-3]. These compounds have carcinogenic and mutagenic effects on the human body [3]. This type of pollution has become a critical issue worldwide that requires efficient techniques that utilize environmental treatment systems. Catalytic combustion technology, which can achieve complete catalytic oxidation by converting PVOCs into CO₂ and H₂O with low energy consumption, wide application range, high treatment efficiency, and no pollution, has attracted considerable attention and is undergoing intense study in the research of volatile organic compounds (VOCs) elimination. However, the development of high-efficiency catalytic combustion catalyst is still the key technology to the elimination of VOCs.

The mutual transformation of the Ce⁴⁺/Ce³⁺ ion pair in CeO₂ can effectively promote the “redox” cycle. Transition metal oxides can dissolve into the CeO₂ lattice to form a solid solution, which can promote the formation of oxygen vacancy and improvement of oxy-

gen storage and release capacity for the corresponding Ce-based oxide catalysts. Ce-based oxides have been widely studied in catalysis [4-6]. CuO can dissolve into the CeO₂ lattice to form Ce_{1-x}Cu_xO₂ oxide solid solution catalysts. The lattice defects can be produced in CeO₂ due to the differences in Ce and Cu ionic radius (Cu²⁺ < Ce⁴⁺), which can increase the content of surface-reactive oxygen species and oxygen vacancies and promote the migration rate of bulk oxygen in the corresponding catalyst. The high oxygen storage and desorption ability can improve catalytic oxidation performance [5,7]. Using the traditional precipitation and wet impregnation methods, CuO cannot effectively dissolve into the CeO₂ lattice to form a uniform CeCu oxide solid solution and isolated transition metal oxide phases, which can affect the generation of oxygen vacancies and decrease the strong interaction between CeO₂ and CuO, restricting the catalytic properties of the Ce_{1-x}Cu_xO₂ oxide solid solution catalyst. Therefore, the CuO effectively dissolved into CeO₂ lattice to form a uniform Ce_{1-x}Cu_xO₂ solid solution to fully promote the catalytic performance of Ce_{1-x}Cu_xO₂ oxide solid solution catalysts, which has attracted considerable attention in the catalysis and materials field.

This study aimed to synthesize Ce_{1-x}Cu_xO₂ oxide solid solution catalysts under mild conditions by one-pot complex methods with different Ce/Cu mole ratios. The influence of the Ce/Cu mole ratio on the physical and chemical properties was investigated. The synthesized Ce_{1-x}Cu_xO₂ oxide solid solution catalysts were used in the catalytic elimination of PVOCs (benzene, toluene, xylene, and ethylbenzene) from air. The physical and chemical properties of the Ce_{1-x}Cu_xO₂ oxide solid solution catalysts on the catalytic elimination of PVOCs were also examined. The Ce_{1-x}Cu_xO₂ oxide solid solution catalysts were then characterized by X-ray diffraction (XRD),

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X-ray photoelectron spectroscopy (XPS), and H₂ temperature-programmed reduction (H₂-TPR) analyses.

EXPERIMENTAL

1. Ce_{1-x}Cu_xO₂ Catalyst Preparation

In a typical complex-method synthesis of Ce_{1-x}Cu_xO₂ oxide solid solution catalyst, stoichiometric Cu(NO₃)₂·3H₂O, Ce(NO₃)₃·6H₂O, and citric acid (CA) (Ce/Cu molar ratio=2.0; CA/(Ce+Cu) molar ratio=1.8) were dissolved in a certain amount of deionized water. The mixture was then stirred at 80 °C until the deionized water completely evaporated. Afterwards, the sample was dried in a constant temperature oven at 90 °C for 24 h, and then the obtained solid sample was calcined at 350 °C for 3.0 h in air. The Ce_{1-x}Cu_xO₂ oxide solid solution catalyst was then obtained and designated as CeCu2. The CeCu3 and CeCu4 catalysts were prepared at the Ce/Cu molar ratio of 3.0 and 4.0, respectively.

2. Catalyst Characterization

2-1. XRD Characterization

X-ray diffraction (XRD) patterns were recorded on a SHIMADZU X-ray diffractometer (XRD-6100 model) with a rotating anode using Ni filtered Cu K α (as radiation source (λ =0.15418 nm) radiation at 40 kV of a tube voltage and 20 mA of a tube current. The data of 2θ from 20° to 80° range were collected with the step size of 0.02° at the rate of 3°/min.

2-2. XPS Characterization

The chemical states of Ce, Cu and O in the prepared CeCu oxide catalysts were certified by the X-ray photoelectron spectroscopy (XPS) measurements. The signals were collected by a KRATOS X-ray sources with an aluminum crystal, operating at 12 kV anode voltage and 12 mA emission current, was used to generate the required Al K α radiation. Curve fitting and background subtraction were performed using Casa XPS software.

2-3. H₂-TPR Studies

H₂ temperature programmed reduction (H₂-TPR) was conducted using a conventional apparatus equipped with a TCD detector. 20 mg of samples were placed in a quartz tube (4.0 mm ID), and then TPR was performed by heating the samples at 10 °C·min⁻¹ from 50 to 400 °C in a 5% H₂-Ar mixture flowing at 25 ml·min⁻¹.

3. Catalytic Activity Measurement

Catalytic tests of all catalysts were carried out in a continuous flow fixed-bed quartz tubular reactor (i.d. 6 mm) under atmospheric pressure. The quartz tube reactor containing 50 mg catalyst was placed inside a tubular furnace. The air was passed downward through the reactor containing the catalyst bed, while an electronic mass flow controller (D07-7A/ZM, China) was used to control air flow rate. The feed gas was obtained by bubbling air through a saturator, which contains PVOCs (benzene, toluene, xylene, and ethylbenzene) in liquid phase, kept at constant temperature to achieve the feed gas mixture consisting of gaseous PVOCs (1.0 vol%) and the feed gas was led over the catalysts at a flow rate of 55 mL·min⁻¹, equivalent to a gas mass space velocity of 66,000 mL·g⁻¹·h⁻¹. Catalytic activity tests were performed in a temperature range of 210–250 °C, which was measured using a thermocouple projecting into the catalyst bed. The reaction temperature was monitored by a temperature programmable controller (ÜGU, model 708P, China) at a

heating rate of 10 °C·min⁻¹ until the given temperature. Before each test, the catalyst bed was heated to the preconcerted temperature point at a heating rate of 10 °C·min⁻¹, and then the feed gas was switched to the catalyst bed and stabilized for 120 min to record the data for the effluent gas interval 5 min. The quantity of PVOCs in the feed gas and reaction products gas were monitored by using on-line gas chromatograph (GC 6890II), equipped with an FID. And the PVOCs conversion can be obtained by the following formula: Conversion (%) = $\frac{C_{In} - C_{Out}}{C_{In}} \times 100\%$ (C_{In} , the PVOCs concentration in the feed gas; C_{Out} , the PVOCs concentration in the products gas.).

RESULTS AND DISCUSSION

1. XRD Characterization

Fig. 1 presents the XRD patterns of the Ce_{1-x}Cu_xO₂ oxide solid solution catalysts with the Ce/Cu mole ratios of 2.0, 3.0, and 4.0, respectively, which were prepared at 350 °C for 3.0 h.

The XRD diffraction peaks were observed at 28.5°, 33.1°, 47.5°, 56.3°, 59.1°, 69.4°, and 76.7° for the prepared CeCu oxide catalysts, which agreed with the fluorite structure of the cubic CeO₂. Moreover, the XRD diffraction peak intensity increases with the increasing Ce/Cu mole ratio. The weak XRD diffraction peaks of CuO at 35.56° and 38.68° are observed for the prepared CeCu2, CeCu3, and CeCu4 oxide solid solution catalysts.

XRD results show that the Ce_{1-x}Cu_xO₂ oxide solid solution is the main formation in the prepared CeCu oxide catalysts. The result confirmed that the Ce_{1-x}Cu_xO₂ oxide solid solution can be effectively prepared by one-step complex method under mild experimental conditions. The ratio of Cu/(Ce+Cu) in the prepared Ce_{1-x}Cu_xO₂ oxide solid solution catalysts is greater than 0.20, which indicates that the prepared Ce_{1-x}Cu_xO₂ oxide solid solution catalysts contain a large number of Cu species. However, the weak CuO crystal phase XRD diffraction peak can be attributed to a large number of CuO species dissolved in the CeO₂ lattice to form Ce_{1-x}Cu_xO₂ oxide solid solution or part of CuO species with high dispersion or amorphous form in the prepared CeCu oxide catalysts. The Ce_{1-x}Cu_xO₂ oxide

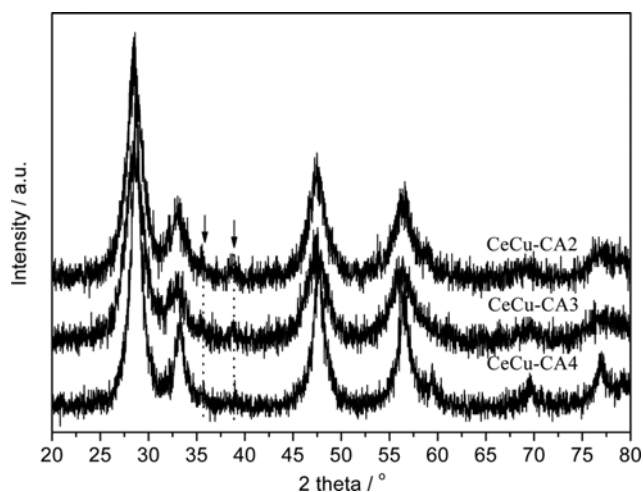


Fig. 1. XRD patterns of the CeCu oxide catalysts.

solid solution catalysts were prepared by citric acid complexation method, and the citric acid complexing agent can react with metal ions (Cu^{2+} , Ce^{4+}) to form the complex compound, providing favorable conditions for Cu species to dissolve into the CeO_2 lattice effectively. Therefore, the Cu species mainly exist in the form of $\text{Ce}_{1-x}\text{Cu}_x\text{O}_2$ oxide solid solution in the prepared CeCu oxide catalysts. The formation of the $\text{Ce}_{1-x}\text{Cu}_x\text{O}_2$ oxide solid solution can improve the strong interaction between CuO and CeO_2 to be produced, which can result in obvious differences in properties compared with the component CuO and CeO_2 existing in isolate formation [8]. The strong interaction between CuO and CeO_2 can weaken the “Cu-O” and “Ce-O” bonds and promote the breaking of the metal-oxygen bonds to produce highly reactive oxygen species. On the other hand, the $\text{Cu}^+/\text{Cu}^{2+}$ and $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox ion pairs can be formed in the $\text{Ce}_{1-x}\text{Cu}_x\text{O}_2$ oxide solid solution catalyst system, which can provide favorable conditions for the fast migration and active sites regeneration of electrons and oxygen ions [2,9]. From the XRD results, the CeCu oxide catalysts exhibited weak CuO crystal diffraction peaks, which indicates that a small amount of crystalline CuO was formed in the prepared CeCu oxide catalysts. The results can be attributed to the content of CuO in the CeCu oxide catalyst system exceeding the saturation capacity of CeO_2 lattice to dissolve CuO, which results in the CuO species aggregating to form the crystal CuO in the roasting process. With the increasing Ce/Cu mole ratio, CeO_2 characteristic diffraction peak intensity gradually increased and followed the order: $\text{CeCu4} > \text{CeCu3} > \text{CeCu2}$. The results showed that the crystallinity of CeO_2 crystal can be increased in the roasting process because of the aggregation of CeO_2 species, which results in the enhancement of the XRD characteristic diffraction peaks. The high Ce/Cu mole ratio will lead to relatively low Cu species content, which is not conducive to the formation of a $\text{Ce}_{1-x}\text{Cu}_x\text{O}_2$ oxide solid solution catalyst. The low Ce/Cu mole ratio will cause a large number of Cu species to form aggregation state crystalline CuO but fully dissolve into CeO_2 lattice. Therefore, the suitable Ce/Cu mole ratio is more favorable for the formation of $\text{Ce}_{1-x}\text{Cu}_x\text{O}_2$ oxide solid solution and activation of the “Cu-O” and “Ce-O” bonds to form reactive oxygen species in the corresponding catalyst.

2. XPS Characterization

Fig. 2 is the XPS spectra of Ce 3d, Cu 2d, and O 1s in the prepared CeCu oxide catalysts. From Fig. 2(a), a series of high-intensity Ce 3d XPS peaks at 882.5, 888.3, 898.1, 900.1, 907.2, and 916.3 eV, attributed to the Ce^{4+} species are observed for the CeCu oxide catalyst [10]. The result indicates that the Ce species in the CeCu oxide catalyst mainly existed in the form of Ce^{4+} , which is consistent with the characterization of XRD. From Fig. 2(b), a series of high-intensity Cu 2d XPS peaks at 933.8, 942.1, 953.9, and 962.3 eV are attributed to the Cu^{2+} species [11]. The Cu species in the CeCu oxide catalyst mainly existed in the form of Cu^{2+} . The Ce and Cu species in the CeCu oxide catalyst system are in the form of high valence states which can improve the lattice oxygen content to achieve a maximum value, providing a material basis for the formation of highly reactive oxygen species.

From Fig. 2(c), a series of O 1s XPS peaks with different intensities are observed at 529.3, 530.7, and 531.8 eV and attributed to three different oxygen species. The lattice oxygen (O_{Latt}) character-

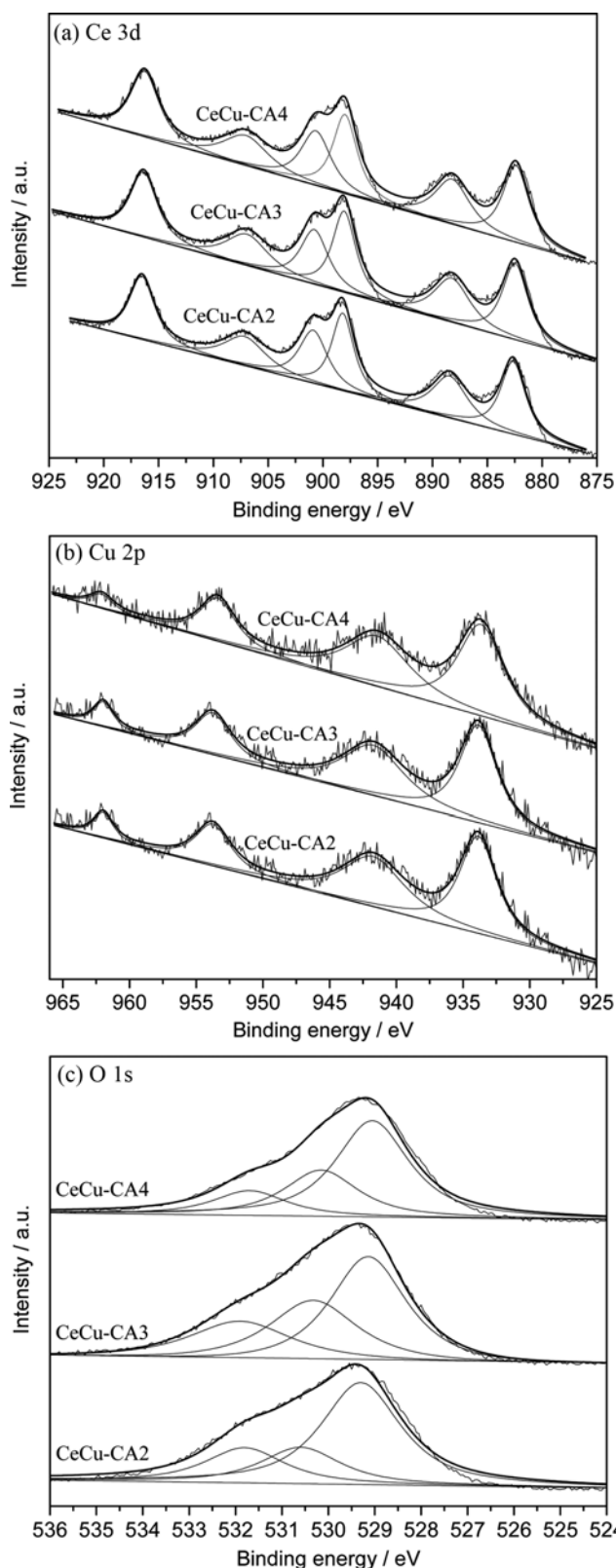


Fig. 2. XPS spectra of Ce 3d (a), Cu 2p (b) and O 1s (c) for the CeCu oxide catalysts.

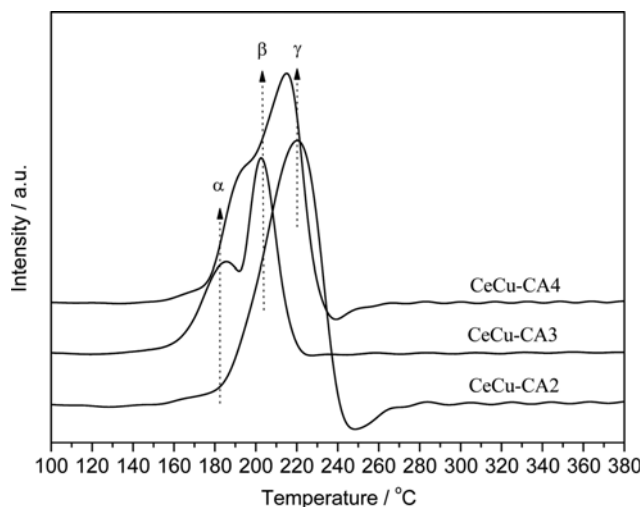
istic XPS peak was observed at 529.3 eV. A large amount of lattice oxygen is present in bulk of the CeCu oxide catalyst, which acts as

Table 1. O1s XPS analysis results of the prepared CeCu oxide catalysts

Catalysts	Species	Percent/%
CeCu-CA4	O _{Latt}	72.4
	O _{OH}	21.0
	O _{ads}	6.6
CeCu-CA3	O _{Latt}	57.6
	O _{OH}	29.9
	O _{ads}	12.5
CeCu-CA2	O _{Latt}	77.7
	O _{OH}	10.9
	O _{ads}	11.4

oxygen storage [12]. The surface-adsorbed oxygen (O_{ads}) was observed at 530.7 eV, which mainly exists on the surface of the catalyst with weak metal atom bonding interaction. Therefore, this kind of surface-adsorbed oxygen species has high catalytic oxidation activity for catalytic oxidation or combustion reaction [12]. This kind of oxygen species can react with organic molecules at low reaction temperatures, and become the main reactive oxygen species in the PVOCs catalytic combustion reaction. The O 1s XPS peak at 531.8 eV is mainly attributed to the oxygen species in the hydroxyl group (O_{OH}) [13,14]. From Fig. 2(c), the Ce/Cu ratio changes can lead to the change of all kinds of oxygen species content in the studied CeCu composite oxide catalysts. The surface oxygen species content of the CeCu3 oxide catalyst was significantly higher than that of the CeCu2 and CeCu4 oxide catalysts. Therefore, the CeCu3 oxide catalyst is more favorable to provide a large amount of reactive oxygen species for PVOCs catalytic combustion at low temperature conditions.

Table 1 shows that the surface lattice oxygen species content was 77.7%, 57.6%, and 72.4% for the CeCu2, CeCu3, and CeCu4 oxide catalysts, respectively. The surface-adsorbed oxygen species content was 11.4%, 12.5%, and 6.6%, respectively. The surface hydroxyl oxygen species content was 10.9%, 29.9%, and 21%, respectively. The surface lattice oxygen species content of the CeCu2 and CeCu4 oxide catalysts was higher than that of the CeCu3 oxide catalyst, but the surface-adsorbed oxygen and hydroxyl group species content of the CeCu3 oxide catalyst was obviously higher than that of the CeCu2 and CeCu4 oxide catalysts. A large number of adsorbed oxygen species exist on the surface of the studied CeCu oxide catalysts, which can be attributed to the CuO species dissolving into CeO₂ lattice to form solid solution and improve the production of the surface oxygen vacancies. The formation of oxygen vacancy can provide favorable conditions for the adsorption and activation of oxygen molecules, and promote the formation of adsorbed oxygen species on the surface of CeCu oxide catalysts [14]. The CeCu3 has obviously higher surface-adsorbed oxygen species content compared with that of the CeCu2 and CeCu4 oxide catalysts, based on the results showing in Table 1. The formation of a large number of surface-adsorbed oxygen species is beneficial to the production of a large number of reactive oxygen species, which can improve the PVOCs catalytic combustion activity for the corresponding catalyst.

**Fig. 3.** TPR patterns of the CeCu oxide catalysts.

3. H₂-TPR Studies

The reducibility of the prepared CeCu oxide catalysts can be studied by H₂-TPR, and the H₂-TPR results are shown in Fig. 3.

Fig. 3 shows that the H₂-TPR curves of the studied CeCu oxide catalysts significantly deviated from the baseline at the reduction temperature of 125 °C. With the increase of the reduction temperature, two distinct intensities of H₂-TPR hydrogen consumption peak α and β were formed in the reduction temperature range of 125 °C to 250 °C for the CeCu3 and CeCu4 oxide catalysts, and the peak intensity and peak area is α < β. The CeCu2 oxide catalyst only formed an obvious hydrogen consumption peak γ at 225 °C.

The reduction temperature of the studied CeCu oxide catalysts was significantly lower than that of the pure phase CeO₂ (approximately 480 °C) and CuO (approximately 300 °C) [15]. XRD results confirmed that the Cu species can be dissolved into the CeO₂ lattice to form CeCu oxide solid solution. The strong interaction between CeO₂ and CuO in the CeCu oxide solid solution can effectively weaken the “Cu-O” and “Ce-O” bonds, improving the reducibility of the metal oxide in the CeCu oxide catalysts. Therefore, the CeCu oxide catalysts have better low-temperature reducibility than that of the pure phase CeO₂ and CuO phase. XPS characterization results indicate that the presence of a large amount of reactive oxygen species on the surface of CeCu oxide catalyst can improve the reducibility of the CeCu oxide catalysts.

From Fig. 3, the CeCu2 oxide catalyst with a Ce/Cu molar ratio of 2.0 has higher reduction temperature than that of the CeCu3 and CeCu4 oxide catalysts, which can be attributed to the weak interaction between CuO and CeO₂ in the CeCu2 oxide catalyst. CuO species content exceeded the maximum saturated capacity of the CeO₂ lattice at the Ce/Cu molar ratio of 2.0, which resulted in isolated CuO species aggregation to form crystalline CuO in the CeCu oxide solid solution. The H₂-TPR hydrogen consumption peak γ of the CeCu2 oxide catalyst can be attributed to the formed CeCu oxide solid solution and the highly dispersed CuO existing on the surface of the CeCu2 oxide catalyst and having weak interaction with CeO₂. With the increase of Ce/Cu molar ratio, the hydrogen consumption peaks α and β with different intensities can be formed

for the prepared CeCu3 and CeCu4 oxide catalysts, which were attributed to the reduction of metal oxides with different forms. The hydrogen consumption peak α can be attributed to the reduction of the CuO species which were highly dispersed on the surface of the CeCu oxide catalysts and have strong interactions with CeO₂. The hydrogen consumption peak β can be attributed to the reduction of CeCu oxide solid solution in the studied CeCu oxide catalyst. At the same time, the CeCu4 catalyst has higher reduction temperature than that of the CeCu3 catalyst, which indicates that the CeCu3 catalyst has a higher reducibility than that of the CeCu4 catalyst. As XPS results show in Table 1, the content of adsorbed oxygen species on the surface of the CeCu4 oxide catalyst was significantly lower than that of the CeCu3 catalyst, resulting in its inferior ability to provide reactive oxygen species compared with CeCu3 oxide catalyst to weaken the low-temperature reducibility of the CeCu4 oxide catalyst.

The suitable Ce/Cu molar ratio (Ce/Cu=3.0) is more favorable for the formation of a large number of CeCu oxide solid solutions in the CeCu oxide catalyst, which can promote the oxygen vacancy. The formation of the CeCu oxide solid solutions can promote the interaction between the CuO and CeO₂ species to enhance oxygen species removability in the CeCu oxide catalyst and greatly improve the low-temperature reducibility of the corresponding catalysts [16]. Based on the H₂-TPR study results, the researchers found that the CeCu3 oxide catalyst can provide more reactive oxygen species for the catalytic oxidation under mild conditions. Therefore, the CeCu3 oxide catalyst may exhibit superior catalytic oxidation or combustion reaction performance.

4. Evaluation of Toluene Catalytic Combustion Activity

The prepared CeCu2, CeCu3, and CeCu4 catalysts were used for toluene catalytic combustion activity evaluation. The toluene catalytic combustion activity evaluation results are shown in Fig. 4: the prepared CeCu oxide catalysts have good toluene catalytic activity, and the CeCu3 oxide catalyst shows the best toluene catalytic combustion activity among the studied CeCu oxide catalysts. The toluene catalytic combustion conversion was only 0.1% on the

CeCu3 oxide catalyst at 220 °C. Furthermore, the toluene catalytic combustion conversion can reach 94.3% and 96.8% on the CeCu3 oxide catalyst at 225 and 230 °C, respectively. The CeCu2 oxide catalyst has worse toluene catalytic combustion activity than that of the CeCu3 oxide catalyst. Moreover, the toluene catalytic combustion conversion is 90.2% and 93.5% at the reaction temperature of 235 and 240 °C, respectively. For the CeCu4 catalyst, the toluene catalytic combustion conversion can reach 94.1% and 95.8% until the reaction temperature is 240 and 250 °C, respectively.

For the studied CeCu oxide catalysts, the highest toluene catalytic combustion temperature of 240 °C was significantly lower than the direct toluene combustion temperature of 535 °C in air. Based on the XRD result, the researchers found that CuO can effectively dissolve into CeO₂ crystal to form CeCu oxide solid solution, which can weaken the “metal-O” bonds to produce highly reactive oxygen species. On the other hand, the formation of solid solutions can promote a large number of oxygen vacancies to be formed in the corresponding CeCu oxide catalysts. Not only can the oxygen vacancy provide an active center for the adsorption and activation of oxygen molecules, but also improve the lattice oxygen species to transfer into reactive oxygen species in the process of catalytic reaction, improving the ability of the corresponding catalyst to provide highly reactive oxygen species [15]. XPS and H₂-TPR results confirmed that the CeCu oxide catalyst can provide abundant reactive oxygen species for the catalytic combustion of toluene molecules under mild conditions. Therefore, the toluene molecules clearly exhibited low-temperature flammability on the studied CeCu oxide catalysts.

The prepared CeCu oxide catalysts with different Ce/Cu mole ratios have significant differences in toluene catalytic combustion activity, with their activity order as follows: CeCu3>CeCu2>CeCu4. The result can be attributed to the Ce/Cu mole ratio changing the properties of the corresponding CeCu oxide catalysts. Table 1 shows that the surface-adsorbed oxygen species content on the surface of the studied CeCu oxide catalysts complies with the order: CeCu3>CeCu2>CeCu4. The surface-reactive oxygen species content increases with the increment of the surface-adsorbed oxygen species content. Moreover, the CeCu oxide catalyst has a strong reactive oxygen species supply capacity, which is conducive to the low-temperature combustion of toluene molecules. H₂-TPR results show that the low temperature reducibility of the CeCu3 oxide catalysts is obviously better than that of the CeCu2 and CeCu4 oxide catalysts. The result also further confirms that the CeCu3 oxide catalyst can provide more reactive oxygen species for oxidation reactions under mild conditions, including low-temperature toluene catalytic combustion reaction. At the same time, an appropriate amount of CuO species is beneficial to the formation of CeCu oxide solid solution in the CeCu oxide catalyst, which can enhance the content of oxygen vacancies. The formation of the CeCu oxide solid solution and oxygen vacancies can improve the interaction between oxide species and enhance the ability of the oxygen species diffusion, migration, and formation in the corresponding CeCu oxide catalyst. Therefore, the ability of the corresponding catalyst to supply reactive oxygen species can be improved under mild conditions, which provides favorable conditions for efficient catalytic combustion of toluene molecules on CeCu oxide catalysts at low tempera-

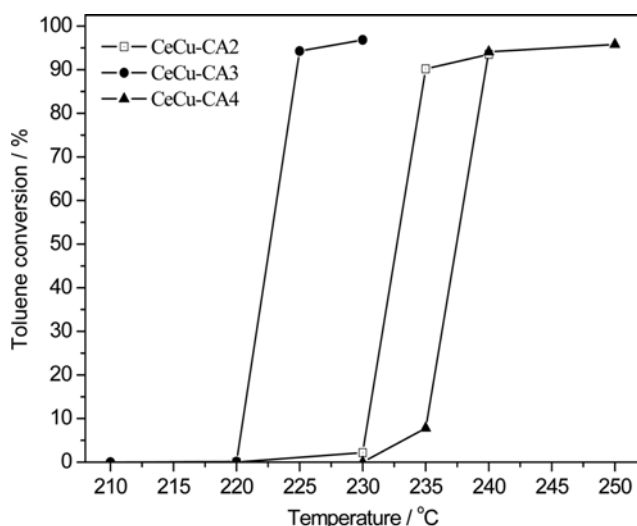


Fig. 4. The effect of Ce/Cu molar ratio on CeCu oxide catalysts catalytic combustion activity.

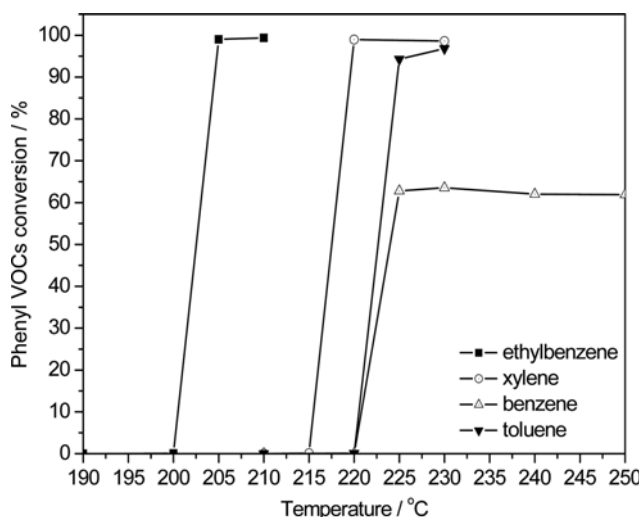


Fig. 5. PVOCs catalytic combustion on CeCu3 oxide catalyst.

ture. Therefore, the CeCu3 catalyst showed the best catalytic activity for toluene catalytic combustion among the studied CeCu oxide catalysts.

5. Evaluation of PVOCs Catalytic Combustion Activity

PVOCs (benzene, toluene, xylene, and ethylbenzene) catalytic combustion properties were tested on the prepared CeCu3 oxide catalyst. The results in Fig. 5 show that the CeCu3 oxide catalyst exhibits excellent catalytic combustion activity for PVOCs especially for ethylbenzene, which showed the best combustibility among the studied PVOCs compounds. The ethylbenzene catalytic combustion conversion was as high as 99% and 99.4% at 205 and 210 °C, respectively. The xylene combustibility is obviously poorer than ethylbenzene on the CeCu3 oxide catalyst, and the xylene catalytic combustion conversion reaches 98.9% and 98.6% at 220 and 230 °C, respectively. However, benzene has the worst combustibility among the studied PVOCs compounds for the CeCu3 oxide catalyst, and the benzene catalytic combustion conversion is only 62.8% and 62.5% at 225 and 230 °C, respectively. The combustibility of toluene is obviously better than benzene for the CeCu3 oxide catalyst, and the toluene catalytic combustion conversion reaches 94.3% and 96.8% at the same reaction temperature. Specifically, the CeCu3 oxide catalyst has different catalytic combustion activities for different PVOCs; the catalytic combustion activity follows the order: ethylbenzene > xylene > toluene > benzene.

Direct combustion temperatures of benzene, toluene, xylene, and ethylbenzene were as high as 562 °C, 535 °C, 500 °C to 528 °C, and 432 °C in air, respectively. The combustion temperatures of benzene, toluene, xylene, and ethylbenzene obviously decrease with the participation of the CeCu3 oxide catalyst, which indicated that the flammability of the corresponding organic compounds was significantly improved when CeCu3 oxide catalyst was used. The CeCu oxide solid solution was formed in the prepared CeCu3 oxide catalyst as confirmed by XRD. The formation of solid solution can weaken the “metal-oxygen” bonds in the studied CeCu3 oxide catalyst, which is beneficial to the formation of the reactive oxygen species. CuO can effectively dissolve in the CeO₂ lattice to form solid solution, which can promote the formation of oxygen vacan-

cies in CeCu oxide solid solution catalyst. The formed oxygen vacancies can provide active sites for the adsorption and activation of O₂ molecules, which can effectively improve the ability of the CeCu3 catalyst to activate O₂ molecules to generate reactive oxygen species [2]. The CeCu3 oxide catalyst has high low-temperature reducibility, which further confirms that the CeCu3 oxide catalyst can provide abundant reactive oxygen species at low temperature for PVOCs catalytic combustion reaction. Therefore, the CeCu3 oxide catalyst exhibits high PVOCs catalytic combustion activity at low reaction temperature.

Differences in the catalytic combustion activity of PVOCs molecules on the CeCu3 oxide catalyst are obvious, which is attributed to the different properties of the PVOCs molecules. Methyl or ethyl substituted on the benzene ring to generate toluene, xylene, or ethylbenzene changes the characteristics of the benzene ring structure, including the dipole moment of benzene molecules, i.e., the dipole moment of benzene, toluene, *o*-xylene, and ethylbenzene are 0, 0.36, 0.62, and 0.59 D [17]. Usually, if the dipole moment of organic compound molecules is large, the polarity of the corresponding organic compound molecules is greater. Furthermore, the polarity of the studied PVOC molecules follows the following order: xylene > ethylbenzene > toluene > benzene. A large number of “metal-oxygen” bonds are found on the surface of CeCu3 oxide catalyst to form the strong polar surface, which is beneficial to the adsorption and activation of the polar organic compound molecules on the surface of the catalyst. Therefore, the adsorption and activation properties of PVOC molecules on the CeCu3 oxide catalyst also follow the following order: xylene > ethylbenzene > toluene > benzene. The adsorption property of benzene molecules on the CeCu3 oxide catalyst is relatively weak; benzene has a highly symmetrical aromatic ring structure to ensure the stability of the structure, which results in the difficulty of activating benzene molecules, reflecting the poor catalytic combustion performance of the CeCu3 oxide catalyst. The hydrogen atom was substituted by methyl or ethyl in benzene ring to produce toluene, xylene, or ethylbenzene, resulting in the changed stability and polarity of the benzene ring structure. The toluene, xylene, or ethylbenzene molecules are easily adsorbed and activated by the CeCu3 oxide catalyst compared with that of benzene molecules. Therefore, the toluene, xylene, and ethylbenzene molecules have higher catalytic combustion activity than that of benzene molecules. Toluene and xylene molecules have different methyl substituent numbers and positions in the benzene ring; xylene molecules suffered more serious damage compared with the toluene molecule. At the same time, the xylene molecular polarity is greater than that of toluene molecules, which can enhance the adsorption and activation capacity of xylene molecule on the CeCu3 oxide catalyst compared with toluene molecule. Therefore, xylene exhibits better flammability compared with toluene on the CeCu3 oxide catalyst. Xylene and ethylbenzene molecules have different properties because of their different substituent, with the xylene molecule having greater molecular size than the ethylbenzene molecules [18]. The steric effect can reduce the adsorption performance of the xylene molecules on the CeCu3 oxide catalyst, which directly leads to the oxidation property of the xylene molecules to be reduced on the surface of the CeCu3 oxide catalyst. The xylene molecule has higher magnetic susceptibility

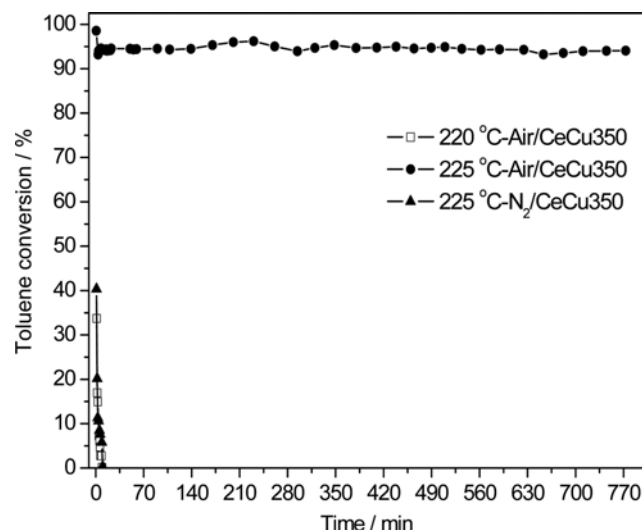


Fig. 6. Relationship between reaction time and toluene catalytic combustion conversion on the CeCu₃ catalyst.

than the ethylbenzene molecule [17]. Therefore, xylene molecules adsorbed on the CeCu₃ oxide catalyst are difficult to be desorbed, which can hinder the CeCu₃ oxide catalyst to adsorb O₂ molecules. The O₂ molecule adsorption capacity can be weakened for the CeCu₃ oxide catalyst, which can reduce the ability of the CeCu₃ oxide catalyst to provide reactive oxygen species for xylene molecule oxidation. Therefore, the CeCu₃ oxide catalyst has better ethylbenzene catalytic combustion performance compared with xylene. Therefore, the flammability of benzene, toluene, xylene, and ethylbenzene on the CeCu₃ oxide catalyst complies with the order: ethylbenzene > xylene > toluene > benzene.

6. CeCu₃ Oxide Catalyst Stability Test

The toluene catalytic combustion stability was tested on the CeCu₃ oxide catalyst. The results are shown in Fig. 6. Reaction temperature can affect the toluene removal efficiency for the CeCu₃ oxide catalyst, as shown in Fig. 6. When the reaction temperature was 220 °C, the toluene removal decreased to 0.1% from 33.7% in 9 min for the CeCu₃ oxide catalyst. When the reaction temperature was 225 °C, the toluene conversion remained above 93% on the CeCu₃ oxide catalysts in 770 min. The toluene removal decreased to 0.1% from 40.3% on the CeCu₃ oxide catalyst at 225 °C in 15 min if the air was replaced by N₂.

O₂ molecules in air cannot directly participate in the catalytic combustion reaction of toluene molecules at low temperature. The toluene removal decreased to 0.1% from 33.7% in 9 min at 220 °C for the CeCu₃ oxide catalyst, which can be attributed to the CeCu₃ oxide catalyst to adsorb toluene molecules. Furthermore, the adsorption of toluene on the CeCu oxide catalyst can achieve adsorption equilibrium in 9 min. Therefore, the toluene removal decreased to 0.1% from 33.7%. Fig. 6 shows that toluene molecules achieve catalytic combustion with the CeCu₃ oxide catalyst and have excellent stability at 225 °C. The CeCu₃ oxide catalyst can adsorb O₂ molecules to achieve O₂ molecules activation to produce reactive oxygen species at a specific reaction temperature. The formation of reactive oxygen species can effectively promote the catalytic combus-

tion of toluene molecules on the CeCu₃ oxide catalyst. Therefore, the CeCu₃ oxide catalyst has high toluene catalytic combustion activity and use stability at 225 °C. The H₂-TPR and Table 1 results confirmed that the CeCu₃ oxide catalyst had abundant reactive oxygen species. Furthermore, the reactive oxygen species is directly involved in the catalytic oxidation or combustion reaction of toluene molecules under certain conditions. However, the toluene removal can reach 40.3% in N₂ atmosphere at 225 °C, which is attributed to the surface reactive oxygen species of the CeCu₃ oxide catalyst involved in the toluene catalytic combustion reaction, adsorbing toluene by the CeCu₃ oxide catalyst. As the catalytic reaction proceeds, the reactive oxygen species can be consumed and the adsorption of toluene reaches equilibrium on the CeCu oxide catalyst. Therefore, the toluene removal decreased to 0.1% in a short time. The result further confirmed that the CeCu₃ oxide catalyst can provide more reactive oxygen species for toluene catalytic combustion reaction to promote toluene molecules highly efficient catalytic removal from air.

CONCLUSION

1. The CeCu oxide solid solution catalyst can be prepared by citric acid one-pot complex method. High-temperature calcination can promote the formation of the CeCu oxide solid solution and promote the strong interaction between CeO₂ and CuO, which can effectively weaken the “metal-oxygen” bonds to improve the reactive oxygen species to be formed on the surface of the corresponding catalyst. Furthermore, the reducibility of the corresponding catalyst can be enhanced. The appropriate Ce/Cu molar ratio is beneficial to the production of strong interaction between Ce and Cu oxides and the formation of a large amount of CeCu oxide solid solution.

2. The CeCu₃ oxide catalyst with Ce/Cu mole ratio of 3.0, which was prepared at 350 °C and calcined for 2 h, exhibited superior catalytic combustion activity of PVOCs. The flammability of PVOCs follows the order: ethylbenzene > xylene > toluene > benzene. The catalytic combustion conversion of ethylbenzene, xylene, toluene, and benzene was 99%, 98.9%, 94.3%, and 62.8% at the reaction temperature of 205, 220, 225, and 225 °C, respectively.

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