Catalytic Oxidation of Trichloroethylene over RuO$_2$ Supported on Ceria-zirconia Mixed Oxide

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Abstract　Ru/Ce-Zr catalysts were prepared by impregnation of Ru on the hydrothermally synthesized Ce-Zr mixed oxide with different molar ratio of Ce/Zr. The resultant products were systematically characterized by inductively coupled plasma(ICP), X-ray diffraction(XRD), scanning electron microscopy(SEM)/energy dispersive spectrometry(EDS), H$_2$-temperature programmed reduction(H$_2$-TPR), NH$_3$-temperature programmed desorption(NH$_3$-TPD) and X-ray photoelectron spectroscopy(XPS). It was proved by H$_2$-TPR and NH$_3$-TPD that the introduction of Ru can improve the activity of oxygen of catalysts and the presence of Zr contributes to the increments of acid properties of catalysts. When the molar ratio of Ce-Zr was 8:4, the quantity of Ru was 0.9%(mass ratio), and the calcined temperature of catalysts was at 400 °C, the removal rate of 90% for trichloroethylene(TCE) was reached at 250 °C for 5360 mg/m^3 TCE and the stability of the catalysts was investigated under the condition. The results showed that the high removal rate can be maintained for at least 90 h, which is promising for industrial application.

Keywords　Catalytic oxidation; Trichloroethylene; RuO$_2$; Ceria-zirconia mixed oxide

1　Introduction

Chlorinated volatile organic compounds(CVOCs), such as dichloromethane(DCM), trichloroethylene(TCE), 1,2-dichloroethane(DCE) and chlorobenzene(CB) are released into the environment from petroleum industries, resin manufacture, plastics production, painting industry, and printing. Owing to their direct(toxic and carcinogenic) and indirect(photochemical smog and depletion in atmospheric ozone) environmental effects, CVOCs are considered the major air pollutants. Therefore, the removal of CVOCs in exhaust gases is of great importance and attracted amount of attention in recent years. So far, adsorption[1—6], photocatalytic degradation[7—10], thermal combustion, non-thermal plasma[11—16] and catalytic combustion[17—20] are studied for the removal of CVOCs. Among them, catalytic combustion is the promising method, as it can realize the complete decomposition of CVOCs and requires less energy consumption[21,22].

In this regard, the ceria-based catalysts have exhibited high efficiency in catalytic combustion of CVOCs owing to their high dissociation ability for C—Cl bonds[17,23—25]. However, the deactivation of ceria by chlorine produced in the combustion process restrains the activity of catalyst[26]. The addition of Zr to the ceria was found to be effective in improving the activity of the catalysts, for example, the removal rate of 90% was achieved at 385 °C for TCE as reported by Gutiérrez-Ortiz *et al.*[27—29]. They also studied the noble metal supported catalysts, including Au, Pt supported on the ceria-zirconia mixed oxides. It was observed that Pt/Ce-Zr catalyst exhibited the higher activity for oxidation of chlorobenzene compared with the ceria-zirconia mixed oxides and the conversion of 90% was achieved with 1.5Pt/Ce-Zr catalyst at 311 °C. On the other hand, the Ru-based catalysts have also emerged as one of efficient catalysts with high activity and can complete oxidation of CVOCs to the end products(CO$_2$, HCl and Cl$_2$) at relatively low temperature. For example, the Ru/Al$_2$O$_3$ catalysts showed higher activity and selectivity for total combustion of TCE compared with the results obtained from Pd and Pt-based catalysts[30]. The Ru-doped ceria catalysts exhibited excellent catalytic activity(with a conversion rate of 90% at 250 °C) and good stability for decomposition of chlorobenzene[31,32]. Although the ceria-zirconia mixed oxide(Ce-Zr) has been widely used as the catalyst support for the treatment of exhaust gases, such as hydrocarbons combustion and VOC oxidation[28,33—35], little attention has been paid to investigate the Ru-doped Ce-Zr catalyst(Ru/Ce-Zr) for TCE decomposition.

In the recent years, it has been proved that respiratory disorders and Parkinson's disease are associated with TCE exposure, which has been classified into the lists of a potential human carcinogen risk[36,37]. It is urgent to effectively deal with TCE. In this study, a series of Ru/Ce-Zr catalysts was synthesized by wet impregnation method, and their performance for catalytic combustion of TCE was investigated by evaluating their activity and long-term stability. The results showed that the introduction of RuO$_2$ can effectively improve the activity of

catalysts and the molar ratio of Ce/Zr in supports had significant influence on the catalytic performance. When 0.9% Ru was doped on the Ce/Zr support with a molar ratio(Ce/Zr) of 2, the high removal rate was obtained. Moreover, the high removal rate can be maintained for at least 90 h. Hence, the Ru/Ce-Zr catalysts are promising for industrial application.

2   Experimental

2.1   Materials

Cerium nitrate[$Ce(NO_3)_3 \cdot 6H_2O$], zirconium(IV) oxychloride($ZrOCl_2 \cdot 8H_2O$), ammonia solution($NH_3 \cdot H_2O$, 25%—28%), trichloroethylene(TCE), hydrochloric acid, nitric acid and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. Rutheniumnitrosyl nitrate[$Ru(NO)(NO_3)_3$] was purchased from Elabscience Biotechnology Co., Ltd. Above reagents except for hydrochloric acid and nitric acid were analytical reagent(AR) and were used without further purification. The aqua regia was guaranteed reagent(GR) from hydrochloric acid(GR) and nitric acid(GR). Deionized water(18.2 MΩ) was obtained from the Milli-Q water purifying system.

2.2   Catalyst Preparation

The ceria-zirconia mixed oxides(Ce-Zr) were synthesized by hydrothermal method using $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrOCl_2 \cdot 8H_2O$ as precursors[38]. The molar ratio(Ce/Zr) of precursors was preliminarily optimized. Typically, 3.47 g of $Ce(NO_3)_3 \cdot 6H_2O$ and 1.29 g of $ZrOCl_2 \cdot 8H_2O$[n(Ce):n(Zr)=8:4] were dissolved in 50 mL of ethanol, and the mixture was stirred at room temperature for 30 min. The ammonia solution(*ca.* 8 mL) was added dropwise in the ceria-zirconia mixed solution until lavender suspension was obtained, and the corresponding pH was in the range of 9—10. Subsequently, the resultant suspension was aged at room temperature for 4 h, and then put into the 100 mL Teflon-lined autoclave, which was kept at 120 °C for 24 h. After cooling to room temperature, the products were purified by washing with acetone solution(50%, volume ratio), then centrifuged at 6000 r/min. The above purification process was repeated three times, followed by the collection of the precipitates settled at the bottom. Finally, the precipitates were dried at 80 °C for 12 h, and calcined in a muffle furnace at 500 °C for 4 h to obtain the ceria-zirconia mixed oxide, which were designated as Ce_2Zr_1. For comparison, the different molar ratio of Ce/Zr(6:6 and 4:8), pure CeO_2 and ZrO_2 were also prepared under the same condition, which were labelled as Ce_1Zr_1, Ce_1Zr_2, CeO_2 and ZrO_2.

A series of Ru-doped catalysts was prepared by the impregnation method[39]. Briefly, 2 g of Ce_2Zr_1 mixed oxide was impregnated in appropriate concentration of the $Ru(NO)(NO_3)_3$ solution to yield a different Ru content[the calculated quantity of 0.5%, 1.0%, 1.5%(mass ratio) for Ru]. The solid materials were collected by centrifuging the solution. Then the precipitates were dried at 100 °C overnight and calcined in air for 4 h at different temperatures(200, 300, 400 and 500 °C). Finally, the Ru/Ce_2Zr_1 catalyst was crushed and sieved to 40—60 mesh for subsequent use. Other catalysts like Ru/Ce_1Zr_1, Ru/Ce_1Zr_2, Ru/CeO_2, and Ru/ZrO_2 were also synthesized as above. The amount of Ru loading was determined by inductively coupled plasma(ICP) and the catalysts were labelled according to actual contents of Ru.

2.3   Catalysts Characterization

The amount of Ru loading was determined by ICP(PerkinElmer Optima 8300). An amount of 100 mg of catalyst was dissolved in the polytetrafluoroethylene vessel by 10 mL of aqua regia(GR) and the sample was digested with microwave digestion method. After digestion, the mixture was heated in 100 mL beaker to remove the acid. Then the remainder was dissolved in 25 mL volumetric flask with ultrapure water for the ICP analysis.

The morphology of the catalysts was characterized on a field-emission scanning electron microscope(FE-SEM, Hitachi, S-4800) under an accelerating voltage of 2.0 kV. The components of the catalysts were analysed with an energy dispersive spectrometer(EDS). Procedures for samples preparation for SEM and EDS: after the catalyst powers were dried at 100 °C for 2 h, they were spread on the sample tray with conductive adhesive, followed by sweeping with rubber suction bulb. Then gold was coated on the catalysts for better electro-conductibility. XRD patterns were obtained from a D8 X-ray diffractometer(Bruker AXS German) using Cu $K\alpha$ radiation over 2θ range of 10°—80° at a scanning rate of 2°/min. XPS analysis was conducted on a Kratos AXIS ULTRA with Al $K\alpha$ X-ray source(1486.6 nm). The photoelectron spectra were calibrated using the C_{1s} signal detected at a binding energy of 284.8 eV from adventitious carbon. Procedures for sample preparation for XPS: spread the catalysts powers on the copper-sheet with carbon conductive adhesive, and swept the copper-sheet with rubber suction bulb. Subsequently, pasted the copper-sheet on the sample tray for characterization of XPS. The catalyst surface area was determined by the BET method from N_2 adsorption isotherms at 77 K by ASAP2020(Micromeritics, USA).

The acidic property of the catalysts was measured by NH_3 temperature-programmed desorption(NH_3-TPD). Briefly, 200 mg of catalyst was purged with the He stream(30 mL/min) for 60 min at 500 °C, after cooling down to 50 °C, the catalyst was saturated with NH_3(10%, volume ratio)/He stream for 120 min, then purged with He stream again to remove excessive NH_3. Subsequently, the catalyst was heated at a rate of 10 °C/min to 600 °C. The consumption of NH_3 was analysed with a thermoconductivity detector(TCD), which revealed the acidic property of the catalysts.

H_2-Temperature programmed reduction(H_2-TPR) was carried out on a Micromeritics AutoChem II 2920 instrument coupled with a thermal conductivity detector(TCD) for examining redox behaviour of catalysts. Catalysts(100 mg) were pre-treated at 500 °C for 1 h and cooled down to 50 °C under the persistent Ar flow(30 mL/min). Then the test was performed by heating the catalysts to 600 °C at 10 °C /min in H_2(10%, volume ratio)/Ar flow(30 mL/min). The consumption of hydrogen was monitored with TCD, which revealed the redox behaviour of catalysts.

2.4 Catalytic Activity Measurements

A schematic diagram of the experiment setup for catalytic performance is shown in Fig.1. The dry clean air from the air source was controlled to be 100 cm³/min with a mass flow controlled. The air as carrier gas flew through the vaporizing chamber and carried the TCE to reach the micro reactor(14 mm i.d., the inset of Fig.1). The liquid TCE was pumped into the vaporizing chamber by syringe pump at a certain rate to obtain 5360 mg/m³ TCE contaminating gas. Along the air stream, the 20—40 mesh SiO_2, 40—60 mesh catalysts(0.4 g of catalyst, 4.6 g of SiC) and 10.0 g of 10—20 mesh SiO_2 were assembled in the micro reactor, which were purged with high-purity N_2 at 400 °C for 1 h to remove the adsorbed species before measurement, and then cooled to 50 °C. The temperature of catalytic oxidation was controlled by the temperature controller system with K-thermocouple. The gas hourly space velocity (GHSV) was maintained at 15000 h⁻¹. The components in the exit stream were adsorbed by total volatile organic compounds (TVOC) adsorption-tube for 20 min and 2 L of the stream passed through the TVOC adsorption-tube. Followed by thermal-desorbing, the sample was analysed in the gas chromatography analyser(GC 9790, Agilent with a FID detector). Separation was conducted using a temperature program with initial temperature of 50 °C, ramping at 3 °C/min to 150 °C, then at 5 °C/min to 250 °C. The conversion of TCE was calculated by the difference between inlet and outlet concentrations according to the Eq.(1). The concentration of product(CO_2) was determined by the CO_2 detector during TCE catalytic combustion over Ru/CeO_2, Ru/Ce_2Zr_1, Ru/Ce_1Zr_1, Ru/Ce_1Zr_2, and Ru/ZrO_2 catalysts.

$$\text{Conversion}_{\text{TCE}}(\%) = \frac{c(\text{in}) - c(\text{out})}{c(\text{in})} \times 100\% \qquad (1)$$

where $c(\text{in})$ and $c(\text{out})$ are the inlet and outlet concentrations of the TCE.

Fig.1   Experimental setup for catalytic activity measurements

3   Results and Discussion

3.1   Optimization of Synthesis Condition

In the present work, the Ru/Ce-Zr catalysts were prepared by wet impregnation method, and three important parameters, *i.e.*, the amount of Ru loading, the molar ratio of Ce/Zr, and the calcination temperature of catalysts were optimized in order to achieve the higher TCE removal rate. As reported in ref.[40], Ce/Zr mixed oxide exhibited good catalytic activity and had been used for the catalytic combustion of chlorinated organic pollutants, so we investigated the optimal molar ratio of Ce/Zr at first. From the results shown in Fig.2(A), the TCE removal rates are enhanced by modifying pure CeO_2 with Zr oxides, and

Fig.2   TCE conversion as a function of temperature over supports with different molar ratio of Ce/Zr(A), and over catlysts with 0.9% Ru-deping and different molar ratio of Ce/Zr(B), with different amount of Ru on Ce_2Zr_1(C) and at different calcined temperatures(D)
TCE concentration: 5360 mg/m³, GHSV: 15000 h⁻¹, catalyst: 400 mg.

the improvement may be attributed to the increase of adsorption of catalysts for TCE[27,41]. In addition, when the molar ratio of Ce/Zr was 8:4, the highest removal rate was reached, indicating the best catalytic activity of Ce/Zr oxide.

After doping with Ru oxide(0.9%, mass ratio), the removal of TCE was further promoted, which is shown in Fig.2(B). The best catalytic performance was obtained on 0.9Ru/Ce$_2$Zr$_1$ catalyst. Removal rate of 90% was readily obtained at 250 °C, which can be attributed to the removal of chlorine in the combustion process by Deacon Reaction.

Fig.2(C) shows that the removal rate increased with the increasing of Ru content from 0.5% to 1.4%(mass ratio) at the treated temperatures. However, the removal rate ranges from 90% to 93% with Ru content from 0.9% to 1.4%(mass ratio). The amplitude is further lower than that with Ru content from 0.5% to 0.9%. Considering the cost of catalysts, 0.9% was selected as the Ru content for subsequent experiments.

The effects of the calcination temperature of the catalysts on the conversion of TCE were also investigated, and the corresponding result is shown in Fig.2(D). As calcination temperature exceeded 300 °C, the high valence Ru(+4) oxides were formed, which facilitated the formation of more oxygen vacancies in the Ru/Ce$_2$Zr$_1$ catalyst[26]. When the temperature was further increased over 400 °C, the oxygen vacancies cannot be increased anymore and the catalytic activity also cannot be increased. So we set the calcination temperature to 400 °C. According to the above experiments, 0.9%Ru catalyst supported on ceria-zirconia mixed oxide was synthesized at 400 °C with a molar ratio of Ce to Zr equalling to 2, which was denoted as 0.9Ru/Ce$_2$Zr$_1$ and exhibited the highest catalytic activity.

The CO$_2$ yields are shown in the Fig.3 at different temperatures over 0.9Ru/CeO$_2$, 0.9Ru/Ce$_2$Zr$_1$, 0.9Ru/Ce$_1$Zr$_1$, 0.9Ru/Ce$_1$Zr$_2$, and 0.9Ru/ZrO$_2$ catalysts. The concentration of CO$_2$ increases with the temperature. It is well known that the higher temperature is favourable to the conversion of TCE. Besides, the highest concentration of CO$_2$ over the 0.9Ru/Ce$_2$Zr$_1$ indicated the best selectivity of CO$_2$.

Fig.3   CO$_2$ yields over Ru-doped catalysts at different temperature
TCE concentration: 5360 mg/m^3; GHSV: 15000 h^{-1}; catalyst: 400 mg.

3.2   Catalyst Characterization

SEM image of 0.9Ru/Ce$_2$Zr$_1$ catalyst is shown in Fig.4 and the inset of Fig.5(A) and the element mappings of O, Ce, Zr and Ru are shown in Fig.5, which confirmed the good dispersion of Ru on the supports. X-Ray diffraction patterns of the supports and Ru-doped catalysts are shown in Fig.6. The diffraction peaks at around 2θ of 28.55°, 33.08°, 47.48° and 59.09° can be ascribed to cubic fluorite structure of CeO$_2$, which are consistent with the results in JCPDS 34-0394[39]. Zr ions were incorporated into CeO$_2$ lattice to form a Ce/Zr solid solution owing to their smaller size, maintaining its fluorite

Fig.4   SEM image of 0.9Ru/Ce$_2$Zr$_1$ catalyst

Fig.5   Characterization of morphology and components for 0.9Ru/Ce$_2$Zr$_1$ catalyst
(A) O; (B) Ce; (C) Zr; (D) Ru. Inset of (A): SEM image of 0.9Ru/Ce$_2$Zr$_1$ catalyst.

structure with cubic symmetry. This is why the diffraction peaks of ZrO$_2$ crystalline phase cannot be observed in Fig.6(A). In addition, the diffraction peak at 2θ of 28.55° shifts to the high angle with the increase of Zr content. Presumably this is because that Ce^{4+} ions(r=0.098 nm) in the CeO$_2$ supports were partially replaced by the small-sized Zr^{4+}(r=0.084 nm) ions, which caused the shrank of cell[42—44]. After the introduction of Ru oxides, no new crystalline phase corresponding to RuO$_2$ can be detected on the support surface, which may be ascribed to the low content and good dispersion of Ru species on the

Fig.6   XRD patterns of a series of supports(A) and Ru-doped Ce$_2$Zr$_1$ with different amounts of Ru(B)

surface of Ce$_2$Zr$_1$ substrate[31], which was also proved in the mapping of Ru in the Fig.5(D).

The XPS analyses were carried out and the results are shown in Fig.7. The signals of Ru$_{3d}$, Ce$_{3d}$, Zr$_{3d}$ and O$_{1s}$ in the 0.9Ru/Ce$_2$Zr$_1$ catalyst can be seen from Fig.7(A). In the XPS spectrum of Ru$_{3d}$[Fig.7(B)], two pairs of peaks appear at 281.4, 282.6 eV and 285.8, 286.9 eV, which can be ascribed to the binding energies of the $3d_{3/2}$ and $3d_{5/2}$ electrons of Ru, respectively. Moreover, the oxidation states of the Ru species were analysed by fitting the curve of Ru$_{3d}$ spectra. Namely, the peak at 281.4 eV in the Ru$_{3d5/2}$ region and the corresponding peak in Ru$_{3d3/2}$ at 285.8 eV are ascribed to the Ru^{4+}. Similarly, the peaks at 282.6 and 286.9 eV could be assigned to the contribution of Ru^{6+}. Ru^{4+} ions tend to be responsible for the increase of oxygen vacancies concentration, and subsequently affect the performance of catalysts[31,45]. In Fig.7(C), the six peaks appearing at 881.9, 885.0, 895.4, 897.8, 904.8 and 913.7 eV can be ascribed to the responses of Ce^{4+}, while two peaks observed at 879.5 and 895.9 eV are the characteristics of Ce^{3+}[31,46]. The results of composition analysis from XPS data are listed in Table 1, and 0.9Ru/Ce$_2$Zr$_1$ catalyst has the higher content of Ce^{3+} than that in 0.9Ru/CeO$_2$, which can induce the formation of oxygen vacancies[47]. The O$_{1s}$ spectrum can be fitted to three peaks, which are assigned to three states of surface oxygen[Fig.7(D)]. The binding energy of 526—530.0 eV is the typical signals of lattice oxygen(O$_{latt}$), and two shoulder peaks at 531 and 533 eV are observed, which can be attributed to the surface-adsorbed oxygen(O$_{ads}$)[48]. The oxygen content in 0.9Ru/Ce$_2$Zr$_1$ is higher than that in 0.9Ru/CeO$_2$, suggesting that the former catalyst has higher oxidation performance. After the addition of Zr oxide, the binding energy of O$_{latt}$ in the catalyst shifts to high value, presumably due to "Zr←O" electron-transfer processes[47].

Fig.7   XPS spectra of Ru/Ce$_2$Zr$_1$ catalyst(A), peak fitting of C$_{1s}$ and Ru$_{3d}$ for Ru/Ce$_2$Zr$_1$(B), Ce$_{3d}$ in 0.9Ru/CeO$_2$ and 0.9Ru/Ce$_2$Zr$_1$ catalysts(C) and O$_{1s}$ in 0.9Ru/CeO$_2$ and 0.9Ru/Ce$_2$Zr$_1$ catalysts(D)

Table 1 XPS analysis of the surface chemical states of catalysts

Catalyst	Ru/CeO_2	Ru/Ce_2Zr_1
Ce^{3+}(%)	18.7	26.6
O_{ads}(%)	33.9	40.1

The acid properties of the catalysts were measured by NH_3 temperature-programmed desorption(NH_3-TPD) analysis. The corresponding TPD profiles are shown in Fig.8, and the quantitative data are summarized in Table 2. The desorption-temperature relationship in the TPD profiles was assumed to analyse the relative strength of acid sites, and the amount of desorbed NH_3 was taken as the total content of acid sites[49—51]. The desorption-temperature performance of the catalysts follows the order of $0.9Ru/Ce_2Zr_1$>$0.9Ru/Ce_1Zr_2$>$0.9Ru/CeO_2$>Ce_2Zr_1>$0.9Ru/Ce_1Zr_1$, which indicates the different performance of adsorption for TCE. The amount of desorbed NH_3 per gram follows the order of Ce_2Zr_1>$0.9Ru/Ce_1Zr_2$>$0.9Ru/Ce_1Zr_1$>$0.9Ru/Ce_2Zr_1$>$0.9Ru/CeO_2$. The amount of desorbed NH_3 markedly increases with the addition of Zr oxide. The Ce_1Zr_2 and $0.9Ru/Ce_1Zr_2$ with the highest content of Zr possess the higher acidity and medium adsorption for TCE. The $0.9Ru/Ce_2Zr_1$ possesses the strong adsorption for TCE and medium quantity of acid sites. The catalytic activity follows the order of $0.9Ru/Ce_2Zr_1$>$0.9Ru/Ce_1Zr_1$>$0.9Ru/Ce_1Zr_2$>$0.9Ru/CeO_2$>Ce_2Zr_1[shown Fig.2(B)], which suggests the activities of catalysts are related to the performance of adsorption and the quantity of the acid sites. Additionally, the introduction of Ru oxides into support causes the decrease in catalyst acidity compared with that of the pure Ce_2Zr_1 owing to the coverage of acid sites by Ru oxides, *i.e.*, the amount of desorbed NH_3 is 0.475 mmol/g for Ce_2Zr_1 and decreases to 0.379 mmol/g for $0.9Ru/Ce_2Zr_1$(as listed in Table 2). These results suggest that the amount of Zr and Ru should be carefully controlled to obtain the catalyst with optimum performance.

Fig.8 NH_3-TPD profiles of support and catalysts

Table 2 Main physical and structural properties of catalysts

Catalyst	Ce_2Zr_1	$0.9Ru/Ce_2Zr_1$	$0.9Ru/Ce_1Zr_1$	$0.9Ru/Ce_1Zr_2$	$0.9Ru/CeO_2$
H2-TPR peak temperature/°C	487	99.0	101	113	88.0
Amount of desorbed NH_3 by NH_3-TPD[a]/(mmol·g^{-1})	0.475	0.379	0.422	0.437	0.226
Amount of hydrogen consumption by H_2-TPR[b]/(mmol·g^{-1})	0.126	0.451	0.429	0.393	0.140
BET surface area/(m²·g^{-1})	88	79	75	69	80

a. Corresponding to total peak area between 50 and 600 °C; *b*. corresponding to total peak area between 50 and 300 °C.

The hydrogen temperature-programmed reduction(H_2-TPR) profiles of catalysts are shown in Fig.9, and the amounts of hydrogen consumption of all samples are listed in Table 2. The H_2-TPR temperature corresponding to peak maximum reflected the reduction performance of catalysts, *i.e.*, the lower temperature and stronger peak, the stronger reduction property of catalysts, and consequently the better catalysts performance. The high-temperature peak(487 °C) can be observed for the support Ce_2Zr_1 that is corresponded to lattice oxygen species of Ce_2Zr_1[52,53]. After the introduction of Ru into catalysts, the position of peaks shift to low temperature, which indicates the more active oxygen(surface oxygen) in the Ru-doped catalysts. With the increase of ZrO_2 in support, the peeks shift to high temperature(*i.e.*, $0.9Ru/Ce_1Zr_1$) and become weaker(*i.e.*, $0.9Ru/Ce_1Zr_1$ and $0.9Ru/ZrO_2$), which suggest the lower activity of

oxygen. The results of H_2-TPR coincide with the catalytic performance[shown in Fig.2(A) and (B)]. These facts can probably be derived from the strong interaction of RuO_2 species with the Ce_2Zr_1 support with higher Zr content and the change in the natures of supports(the doping of Zr into CeO_2)[54]. The temperature peak maximum of Ru/CeO_2 is the lowest, the peak is weaker and broader, resulting in poor catalytic performance. The hydrogen consumption in Table 2 for the low-temperature peak can be used as reference of the activity of oxygen, which are consistent with the activities of catalysts, as shown in Fig.2.

The surface areas of the catalysts are presented in Table 2. After the introduction of Ru into the catalysts, the surface area decreases, which could be attributed to the partial coverage of the catalyst surface by ruthenium oxide. The BET surface area of Ce_2Zr_1 is 88 m²/g, which is greater than that of Ru-loaded catalysts. For example, the value of Ru/Ce_2Zr_1 decreases to 79 m²/g. Moreover, the surface area of the catalysts is decreased slightly with the addition of Zr oxide. However, the catalytic activity is depended on the incremental acid sites and the surface area, which explain why the $0.9Ru/Ce_2Zr_1$ exhibits the highest acti-vity in the Fig.2(B).

3.3 Reaction Mechanism

It is well known that the abatement of CVOCs involved four steps. The first step is the adsorption of the chlorinated molecule on the acid sites of catalysts[31]. The incorporation of ZrO_2 into CeO_2 lattice can be beneficial to increase the acidic

Fig.9 H_2-TPR profiles of support and catalysts

sites, as proved in the results of NH$_3$-TPD. In the second step, the Ce^{3+}/Ce^{4+} acts as active centres for C—Cl bonds splitting[33]. Consequently, the dissociative CH$_x$ species are oxidized by the active oxygen species to produce H$_2$O and CO$_2$ through a Mars-van Krevelen mechanism[40,55]. Meanwhile, the dissociative Cl species can be removed and oxidized to form Cl$_2$ *via* Deacon reaction, otherwise, the adsorption of Cl species on the active sites could cause the rapid deactivation of catalysts. After the introduction of Ru oxides, the dissociated Cl can be removed rapidly from the active sites of catalysts, and results in the improved activity. Finally, the catalysts recover when the Cl and the other species are removed off the surface of catalysts. The process of mechanism is described in the Fig.10.

Fig.10   Diagram of reaction mechanism for the catalytic combustion for TCE

We further investigate the stability of support and catalysts at 250 °C with the GSHV of 15000 h^{-1}, and the results are shown in Fig.11. It is obvious that the catalytic conversion of Ce$_2$Zr$_1$ support for TCE was about 40% within the investigated time of 90 h. After the addition of Ru oxides, catalysts exhibit substantially higher catalytic activity than Ce$_2$Zr$_1$. Among the tested catalysts, the 0.9Ru/Ce$_2$Zr$_1$ catalyst shows the highest catalytic performance, and these results are consistent with the above mentioned mechanism.

Fig.11   Stability tests over Ce$_2$Zr$_1$ support and Ru-doped catalysts

4   Conclusions

A series of Ru/Ce-Zr catalysts was prepared by impregnation method and characterized by XRD, N$_2$-adsorption, SEM,

EDS, XPS, NH$_3$-TPD and H$_2$-TPR. The characterization results indicated that 0.9Ru/Ce$_2$Zr$_1$ catalyst possessed the highest Ce^{3+}(26.6%) and adsorbed O(40.1%), and redox properties. Subsequently, the catalytic combustion of TCE on the Ru/Ce-Zr catalysts were investigated by evaluating their activity and long-term stability. The results showed that the introduction of RuO$_2$ could effectively improve the activity of catalysts and the molar ratio of Ce/Zr in supports had significant influence on the catalytic performance. When the molar ratio of Ce/Zr was 8:4, the quantity of Ru was 0.9%. And the calcined temperature of catalysts was 400 °C, the removal rate of 90% for TCE was reached, and the stability of the catalysts was investigated under the condition. The results showed the high removal rate could be maintained for at least 90 h, which is promising for industrial application.

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