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Article

Novel synthetic route to Ce-Cu-W-O microspheres for efficient catalytic oxidation of vinyl chloride emissions

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ABSTRACT

The solubility of ammonium tungstate in a special hydrothermal condition is exploited to synthesize uniform microspheres of Ce-Cu-W-O oxides. Compared to their W-undoped counterparts, they possess more Ce³⁺ and oxygen vacancies, thereby promoting oxygen mobility. The formed rich WO₃ surface can effectively provide acid sites, which is helpful for adsorption of vinyl chloride and interrupting the C-Cl bond. In addition, the presence of WO₃ induces the formation of finer CuO nanoparticles with respect to the traditional coprecipitation method, thereby resulting in a better reducibility. Benefiting from both the enhanced acidity and reducibility, the Ce-Cu-W-O microspheres deliver excellent low-temperature vinyl chloride oxidation activity (a reaction rate of 2.01×10^{-7} mol/(g_{cat}·s) at 250 °C) and high HCl selectivity. Moreover, subtle deactivation occurs after the three cycling activity tests, and a stable vinyl chloride conversion as well as mineralization are observed during the 72-h durability test at 300 °C, which demonstrates good thermal stability. Our strategy can provide new insights into the design and synthesis of metal oxides for catalytic oxidation of chlorinated volatile organic compounds.

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1. Introduction

Volatile organic compounds (VOCs) released by a variety of sources, such as the exhaust gas of factories, petrochemical processes, and vehicle activities, are significant atmospheric pollutants [1–5]. Chlorinated VOCs (CVOs) generate a great negative influence on the atmosphere due to acute toxicity and high environmental stability. It is urgent to alleviate the emission of vinyl chloride (VC) because it is the main raw material used in the industrial production of polyvinyl chloride (PVC) [6–8]. Therefore, numerous technologies including adsorption,

absorption, condensation, thermal oxidation, and catalytic oxidation have been developed to eliminate poisonous gases [9,10]. Among them, low-temperature catalytic oxidation is generally employed as an environment-friendly and efficient way to degrade CVOs.

Noble metal catalysts exhibiting significant activity are limited owing to their high cost and low reserves. In addition, they are often inactivated by Cl poisoning during the catalytic oxidation of CVOs [11,12]. Transition metal oxides play an indispensable role in a wide range of catalysts owing to their high activity, low cost, and outstanding resistance to Cl poisoning.

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The deep catalytic oxidation of VC is significantly affected by acidity and reducibility. The first degradation step of VC is the adsorption and rupture of the lower bonding energy C–Cl bond at the acid site. Then, the C–C, C–H, or C=H bonds are further interrupted at the redox sites, where the intermediates and byproducts are completely destroyed [13–15]. The former involves the adsorption activation of the CVOC reaction molecule, and the latter corresponds to the deep oxidation ability of the catalyst.

Ceria, one of the transition metal oxide catalysts with a high oxygen storage capacity (OSC) and a unique redox property, has attracted remarkable interest in recent years [16,17]. The presence of ceria can increase the migration of lattice oxygen in cerium-included oxide catalysts. However, it exhibits a poor deep catalytic oxidation ability for VOCs. The transformation of Cl species plays a vital role in the activity and selectivity of catalysts. However, ceria is deactivated quickly upon absorption of the Cl₂ or HCl that decompose from CVOCs [18–20]. After the doping process with a transition metal, such as Cu, Co, or Mn, ceria-based oxides exhibited enhanced catalytic activity and stability during CVOC oxidation. For example, CeO₂–CuO [21], Mn–Ce–La [19], and ACeO_x (A=Co, Cu, Fe, Mn, or Zr) [22] are well considered as potential catalysts for the decomposition of CVOCs because of their outstanding redox properties. The Ce–Cu–O composite is a popular choice, but it is still unsatisfactory because of weak surface acidity.

It was reported that TiO₂ and zeolite (ZSM-5, SBA-15) can offer acid sites. However, the introduction of zeolite often results in a high price and poor reducibility [23]. Tungsten oxide has a unique acidity, which is usually stronger than that of common solid acid oxides, such as SiO₂–Al₂O₃, H₃PO₄/SiO₂, and molecular sieves [24,25]. Thus, based on guaranteeing reducibility, the acidity can be enhanced by adding a small amount of tungsten oxide into the Ce–Cu–O composite. Recently, Wang et al. [26] successfully loaded WO_x on the surface of CeO₂ by impregnation, promoting both acidity and reducibility. Nevertheless, it requires a two-step calcination process, probably weakening the interaction between the active component and W species. Wang et al. [27] found that the interaction of WO_x with the CeO₂ and Pt species led to the formation of W–O–Ce and Pt–O–W, of which W–O–Ce increased oxygen vacancies and acidity, while Pt–O–W promoted the reducibility and availability of surface oxygen. Zhang et al. [28] found that the hydrothermal method can synthesize a uniform WO₃/TiO₂ composite, where W species entered the lattice of TiO₂, which in turn favored the generation of fine-sized TiO₂. One phenomenon that should be focused on is that acid sites are mostly distributed in the bulk phase. To better activate the C–Cl bond of VC molecules, acid sites should be located on the catalyst surface. However, creating a catalyst with rich surface WO₃ through a one-step strategy remains a great challenge.

Herein, uniform microspheres of Ce–Cu–W–O catalysts, with rich surface WO₃ and highly dispersed CuO species, were synthesized by an ammonium tungstate involved hydrothermal method. Ammonium tungstate is slightly soluble in water at normal temperature and pressure, but its solubility is greatly improved under hydrothermal conditions. WO₃ was mainly

concentrated on the surface of uniform spheres, providing enough acid sites, which was beneficial to the adsorption of VC and interruption of the C–Cl bond. Besides, the oxidation performance was mostly remained after the three cycling activity tests. Moreover, systematic characterizations, including X-ray diffraction (XRD), N₂ physisorption, scanning electron microscopy energy dispersion scanning (SEM-EDS), H₂ temperature-programmed reduction (H₂-TPR), NH₃ temperature-programmed desorption (NH₃-TPD), Raman, and X-ray photoelectron spectroscopy (XPS), were carried out to unveil the nanostructure formation mechanism and the relationship between the microscopic structure and activity. Our approach, demonstrated in this work, could provide a new avenue to design and synthesize highly effective transition metal oxides as catalysts for eliminating CVOCs emissions.

2. Experimental

2.1. Catalyst synthesis

HM–CeCuW composite oxide catalysts were prepared by a hydrothermal method. Firstly, 4 mmol Ce(NO₃)₃·6H₂O (analytical reagent, Sinopharm Chemical Reagent Co., Ltd.), 4 mmol Cu(NO₃)₃·3H₂O (analytical reagent, Sinopharm Chemical Reagent Co., Ltd.), 5% (NH₄)₁₀W₁₂O₄₁·xH₂O (99.95%, Macklin), and 4 mmol polyvinyl pyrrolidone (PVP, *M_w* = 58000 g/mol, Aladdin) were dissolved in 15 mL distilled water under vigorous stirring for 10 min. Meanwhile, 20 mmol urea (analytical reagent, Sinopharm Chemical Reagent Co., Ltd.) and 4 mmol PVP were dissolved in 15 mL distilled water under vigorous stirring for 10 mins in another beaker. Secondly, the two solutions were mixed together and kept stirring for another 10 mins at room temperature. After that, 1 mL HNO₃ was added into the obtained solution. Then, the mixed solution was transferred into a 50 mL Teflon-lined autoclave and maintained at 120 °C for 24 h. The resulted mixture was centrifuged three times with ethanol and deionized water and then dried at 70 °C for 24 h. Finally, the residue was taken out and calcined at 400 °C for 4 h to obtain the final catalysts. Furthermore, HM–CeCuW composites were synthesized with different reaction times (1, 3, 6, 12, 18, and 24 h) at 120 °C to observe the growth process of HM–CeCuW microspheres. For comparison, the HM–CeCu composite was synthesized using the same process without adding (NH₄)₁₀W₁₂O₄₁·xH₂O.

CP–CeCuW composite oxides were prepared by a coprecipitation method. Firstly, 4 mmol Ce(NO₃)₃·6H₂O, 4 mmol Cu(NO₃)₃·3H₂O, and 5% (NH₄)₁₀W₁₂O₄₁·xH₂O were dissolved in 30 mL distilled water, followed by adding an appropriate amount of ammonia to adjust the pH of the solution between 4.5 and 6. The resulted mixture was centrifuged three times with ethanol and deionized water and then dried at 70 °C for 24 h. Finally, the dried powder was calcined at 400 °C for 4 h to obtain the final catalyst. The W-undoped CP–CeCu was also synthesized using the same process without adding (NH₄)₁₀W₁₂O₄₁·xH₂O.

2.2. Characterization

XRD patterns of the catalysts were obtained by a Bruker AXS D8 Avance X-ray diffractometer with Cu- $K\alpha$ radiation (range: 10° – 80° , step size: 0.02° , step time: 2 s). A 200 mg powder sample was used to obtain the N_2 physisorption measurements with a BELSORP-mini II instrument. A Hitachi S-4800 operated at 5 kV was used to observe the morphology of samples. The energy dispersive X-ray analysis (EDX) was performed by an EDXA Octane Elect Plus at 15 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed by a Physical Electronics Quantum 2000. Raman spectra were measured on a DXR2xi with a 532 nm laser.

H_2 -TPR and NH_3 -TPD were conducted using a Micromeritics AutoChem II 2920 apparatus assisted by a thermal conductivity detector (TCD). For H_2 -TPR, a 50 mg sample was pretreated with a pure He stream (30 mL/min) at $300^\circ C$ for 0.5 h. After cooling down to room temperature, it was raised to $800^\circ C$ ($10^\circ C/min$) under a 10 vol% H_2/Ar stream (30 mL/min). For NH_3 -TPD experiments, 80 mg samples were saturated with anhydrous NH_3 (4% in He, 30 mL/min) for about 0.5 hour. Then, the catalysts were heated ($10^\circ C/min$) in a He stream (50 mL/min) to desorb NH_3 .

2.3. Activity measurements

The oxidation of VC was chosen to assess the performances of the HM-CeCu, HM-CeCuW, CP-CeCu, and CP-CeCuW composite oxides. Catalytic oxidation experiments were performed as follows: 0.10 g of grain catalyst with a size 30–80 mesh was packed into a quartz reaction tube; then, a gaseous mixture of 1000 ppm VC in dry air was fed at a flow of $30\text{ mL}\cdot\text{min}^{-1}$, with a GHSV of $18000\text{ mL}/(\text{g}_{\text{cat}}\cdot\text{h})$. The temperature was increased in

steps of $25^\circ C$ between 100 and $400^\circ C$, and the cycle was repeated twice using the same catalyst sample. The VC conversion was analyzed using a GC-8A gas chromatograph manufactured by Shimadzu Corporation of Japan, equipped with a packed column and a hydrogen flame ionization detector (FID). The mineralization was carried out using a Thermal Conductivity Detector (TCD). The conversion of VC and mineralization were defined based on the following reaction:

$$\text{VC conversion} = ([C_2H_3Cl]_{\text{in}} - [C_2H_3Cl]_{\text{out}}) / [C_2H_3Cl]_{\text{in}} \quad (1)$$

$$\text{Reaction rate} = (V_{C_2H_3Cl} \times X_{C_2H_3Cl}) / m_{\text{cat}} \quad (2)$$

Reaction rate, $\text{mol}/(\text{g}_{\text{cat}}\cdot\text{s})$;

$V_{C_2H_3Cl}$ is VC flow rate, mol/s ;

$X_{C_2H_3Cl}$ is VC conversion, %;

m_{cat} is the catalyst mass, g.

$$\text{Mineralization rate} = [CO_2]_{\text{out}} / \{([C_2H_3Cl]_{\text{in}} - [C_2H_3Cl]_{\text{out}}) \times 2\} \quad (3)$$

When organic compounds were undetected in the outlet, the concentration of both Cl_2 and HCl was calculated via the gases passing through a NaOH solution (0.0125 mol/L) for 0.5 h. Chemical titration was used to calculate the density in the obtained solution. *N,N*-diethyl-*p*-phenylenediamine (DPD) server was used as the indicator, and ferrous ammonium sulphate (FAS) was used as the titrant. The Cl^{-1} concentration was confirmed by an ion selective electrode. All measurements were repeated three times.

3. Results and discussion

3.1. Catalyst activity

The evaluation results for VC catalytic degradation over the catalysts are shown in Fig. 1(A). It is concluded that W doping

Fig. 1. (A) VC conversion as a function of the reaction temperature over HM-CeCu (1), HM-CeCuW (2), CP-CeCu (3), and CP-CeCuW (4); (B) the mineralization rate of HM-CeCu (1) and HM-CeCuW (2); (C) three-cycle activity test of HM-CeCu (1) and HM-CeCuW (2); (D) durability of VC oxidation over HM-CeCuW at $300^\circ C$ for 72 h.

Table 1

Comparison of VC oxidation performance.

Sample	Reaction rate at 250 °C (mol/(g _{cat} ·s))	GHSV (h ⁻¹)	HCl selectivity at 250 °C (%)	Ref.
Co _{0.7} CeO _x	7.46×10^{-8}	15000	—	[17]
LaCe _{0.2} Mn _{0.8} O ₃	1.78×10^{-7}	15000	—	[30]
1%Ru/COP-4	1.19×10^{-7}	48000	—	[31]
Co ₃ O ₄ -CP-4	1.85×10^{-8}	30000	—	[32]
Co ₃ O ₄ -c	2.96×10^{-8}	48000	93	[33]
HM-CeCu	1.11×10^{-7}	18000	97	This work
HM-CeCuW	2.01×10^{-7}	18000	98	This work

can promote the oxidation activities of HM-CeCu and CP-CeCu, and the hydrothermal method plays a more significant role. Regarding HM-CeCu, HCl selectivity increases from 85% to 97% at 200 °C after doping with WO₃. This is not only due to the expected enhanced acidity, but also to a better low temperature reducibility, as revealed in the H₂-TPR analysis. As a result, HM-CeCuW shows the highest activity. The T₉₀ (the temperature required to reach a 90% conversion of VC) is as low as 250 °C, and the mineralization rate (Fig. 1(B)) at that temperature reaches 99%, demonstrating its superior deep oxidation ability. The reaction rate at 250 °C is 2.01×10^{-7} mol/(g_{cat}·s), which is higher than those reported in the literature (Table 1). To investigate the stability of HM-CeCu and HM-CeCuW, three cycles of testing were performed (Fig. 1(C)). A slight decrease in conversion during the second reaction cycle was found because carbon chloride species adhered to the surface of the catalyst [29]. It should be pointed out that the reaction cycles virtually overlapped in the second and third cycles for HM-CeCuW, suggesting the catalyst is immune to chlorine poisoning. To evaluate the potential application of HM-CeCuW, a durability test with a prolonged time of 72 h was carried out at 300 °C (Fig. 1(D)). The catalyst maintained a stable VC conversion of 90%, which is close to the value of the third cycle test. Also, the mineralization remains near 90%, confirming its good deep oxidation activity.

Fig. 2. XRD patterns of HM-CeCu (1), HM-CeCuW (2), CP-CeCu (3), and CP-CeCuW (4).

3.2. Catalyst characterization

3.2.1. Structural and textural properties

The wide-angle XRD patterns of the HM-CeCu, HM-CeCuW, CP-CeCu, and CP-CeCuW samples are shown in Fig. 2. The reflections at $2\theta = 28.6^\circ, 33.1^\circ, 47.5^\circ$, and 56.3° for the four catalysts are well indexed to the typical cubic fluorite-like structure of CeO₂ (JCPDS No. 04-0593). Main reflections at $2\theta = 35.5^\circ$ and 38.7° can be indexed to CuO (JCPDS No. 48-1548). On the other hand, no intensity peaks characteristic of WO_x species were observed for any of the catalysts, which is probably due to the highly distributed W or its too small content. The crystal sizes of CuO calculated by the Scherrer equation using the (1 1 0) plane are 43.5 nm for HM-CeCu, 11.9 nm for HM-CeCuW, 87.7 nm for CP-CeCu, and 75.8 nm for CP-CeCuW. It is concluded that W doping can restrict the growth of CuO particles via the hydrothermal method, which will result in a better reducibility. This can be correlated to the novel element distribution, which will be discussed in the growth process of HM-CeCuW microspheres.

The nitrogen adsorption/desorption isotherms of the catalysts are presented in Fig. 3(A). All samples present a Type IV

Fig. 3. The N₂ adsorption-desorption isotherms (A) and BJH pore size distribution (B) of HM-CeCu (1), HM-CeCuW (2), CP-CeCu (3), and CP-CeCuW (4).

Fig. 4. SEM micrographs of HM-CeCu (A, E), HM-CeCuW (B, F), CP-CeCu (C, G), and CP-CeCuW (D, H); (I) EDX mapping images of HM-CeCuW; (J, K) EDX analysis of HM-CeCuW and CP-CeCuW in different regions.

isotherm. The curves have a small hysteresis loop in the medium pressure section, indicating the presence of mesopores. The hysteresis loop in a relative pressure (P/P_0) range between 0.5 and 1 illustrates the presence of irregular mesopores from stacking particles [34]. As seen in Fig. 3(B), mesopores range from 10 to 50 nm. Interestingly, upon doping with W, the hydrothermal method induces a larger specific area, whereas coprecipitation plays a negative role. Combined with the results

of the catalytic evaluation, specific surface area is not the key parameter influencing the total VC oxidation.

Scanning electron micrographs of the as-prepared catalysts are presented in Fig. 4(A)–(H). The HM-CeCu and HM-CeCuW have a similar uniform spherical structure. CP-CeCu and CP-CeCuW are composed of random nanoparticles. The HM-CeCu spheres have a mean diameter of 300 nm while the HM-CeCuW ones are 1 μ m. In addition, the formed spheres are uniform. The EDX results of the HM-CeCuW and CP-CeCuW catalysts are shown in Fig. 4(I)–(K). The EDX mapping images show that W, Ce, and Cu are uniform in the microspheres of HM-CeCuW, where W content is the lowest. EDX analysis in different regions (Fig. 4(J), (K)) of the two catalysts were carried out to investigate the material homogeneity. Similar elemental distributions are found in HM-CeCuW samples in different regions, whereas the element content of CP-CeCuW varies greatly.

To reveal the growth process of the HM-CeCuW microspheres, a morphological evolution study of the microspheres with different reaction times was conducted at 120 $^{\circ}$ C. The results of SEM, XRD, and EDX are shown in Fig. 5 and Table 2. During the first hour, most of the ammonium tungstate is insoluble, meanwhile an irregular morphology of CeO_2 is formed (Fig. 5(A)). The mixture of insoluble ammonium tungstate and CeO_2 decomposed from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, as confirmed by XRD and EDX. After the third hour, the surfactant in the solution adsorbs onto the surface of the CeO_2 . The nanoparticles self-assemble to form a solid sphere because this is the lowest activation energy required at this time. The characteristic peaks of CeO_2 and CuO appear in the XRD spectrum, indicating

Fig. 5. SEM micrographs of HM-CeCuW catalysts synthesized via different reaction times: (A) 1 h, (B) 3 h, (C) 6 h, (D) 12 h, (E) 18 h, and (F) 24 h; (G) XRD patterns of HM-CeCuW for different hydrothermal reaction times: (1) 1 h, (2) 3 h, (3) 6 h, (4) 12 h, (5) 18 h and (6) 24 h; (H) the schematic growth process of HM-CeCuW microspheres.

Table 2

Bulk phase atomic ratio of the catalysts from EDX analysis.

Sample	Bulk phase atomic ratio (%)		
	Ce	Cu	W
HM-CeCu-24 h	69.0	31.0	—
HM-CeCuW-1 h	22.0	—	78.0
HM-CeCuW-3 h	59.3	38.3	2.4
HM-CeCuW-6 h	58.5	39.0	2.5
HM-CeCuW-12 h	53.8	44.4	1.8
HM-CeCuW-18 h	58.8	39.2	2.0
HM-CeCuW-24 h	67.0	30.0	3.0

that CuO begins to grow on the sphere. Meanwhile, the diffraction peak of ammonium tungstate disappeared, revealing that ammonium tungstate had been dissolved.

As the hydrothermal time was prolonged to 12 h, the spheres grow due to the gradual production of CuO and CeO₂. The diffraction peak intensity of CuO increases from 6 to 12 h, indicating the accumulation of CuO, which is proved by EDX. Between 12 and 24 h, WO₃ begins to deposit on the surface of the microspheres. From the decreased diffraction intensity of CuO in the XRD pattern and more W content, displayed in Table 2, we conclude that W can induce fine-sized CuO. More importantly, by comparing the atomic ratio of Ce:Cu:W in XPS (48:46:6) and EDX (67:30:3), it can be found that W is rich on the microsphere surface (Table 2). All these results faithfully prove that CeCuW-O microspheres with enriched surface W were successfully synthesized via a simple one pot hydrothermal method by taking the advantage of the solubility of (NH₄)₁₀W₁₂O₄₁·xH₂O.

3.2.2. Acidity and Reducibility

The acidic properties play an important role in the adsorption of VC and its subsequent combustion, which were evaluated by NH₃-TPD (Fig. 6). The profiles can be divided into two sections, 100–200 °C and 200–300 °C, corresponding to adsorbed ammonia on weak and moderate acidic sites, respectively [35]. The desorption area of HM-CeCuW and CP-CeCuW

is much larger than that of HM-CeCu and CP-CeCu. This proves that the introduction of W can enhance the acidity of catalysts [36,37]. Thus, the W-doped catalysts outperform their W-undoped counterparts. Although CP-CeCuW has the largest number of acidic sites, it shows a weaker oxidation activity than HM-CeCuW. This is because VC oxidation performance depends on both acidity and reducibility, and the redox properties will be discussed by the following H₂-TPR.

H₂-TPR analysis was carried out to investigate the influence of W doping on catalyst reductivity. As shown in Fig. 7, the peaks at 140–155 °C belong to the reduction of well-dispersed Cu species and CuO that closely interacted with CeO₂. The peaks at 166–182 °C are attributed to the reduction peak of CuO interacting weakly with CeO₂ [38]. Regarding CP-CeCu, the reduction temperature changes slightly after W doping. Moreover, H₂ consumption is significantly reduced, which means that the introduction of W will reduce the reducibility of CP-CeCuW oxides. This phenomenon is mainly caused by the increased grain size of CuO nanoparticles. In contrast, an apparently lower reduction peak centered at 123 °C appears in HM-CeCuW. It might be assigned to the reduction of small grain sizes of CuO nanoparticles, as evidenced by the XRD analysis, which benefited from the enriched WO₃ on the microsphere surface. After the addition of W into HM-CeCu, both enhanced reducibility and acidity result in the best VC oxidation performance.

3.2.3. Raman and XPS

Based on the advantages of the ammonium tungstate-assisted hydrothermal method, the effect of W on HW-CeCuW properties was studied by Raman (Fig. 8(A)). It is reported that the intensity ratio of the peaks located at 580 and 454 cm⁻¹ (*I*₅₈₀:*I*₄₅₄) can be used to verify the oxygen vacancies of CeO₂ [39]. The *I*₅₈₀:*I*₄₅₄ values are calculated to be 0.04, 0.47, 0.05, and 0.07 for HM-CeCu, HM-CeCuW, CP-CeCu, and CP-CeCuW, respectively. The much larger *I*₅₈₀:*I*₄₅₄ ratio of HM-CeCuW compared to the other catalysts indicates cooperatively positive effects of the W addition and hydrothermal

Fig. 6. NH₃-TPD profiles of HM-CeCu (1), HM-CeCuW (2), CP-CeCu (3), and CP-CeCuW (4).

Fig. 7. H₂-TPR profiles of HM-CeCu (1), HM-CeCuW (2), CP-CeCu (3), and CP-CeCuW (4).

Fig. 8. Raman spectra (A) and Ce 3d (B), O 2p (C), Cu 2p (D), and W 4f (E) XPS spectra of HM-CeCu (1), HM-CeCuW (2), CP-CeCu (3), and CP-CeCuW (4).

route. On the other hand, for HM-CeCuW, the positions of these peaks show a blue-shift compared to HM-CeCu, suggesting increased defects within the basal catalyst [28]. More defective sites will accelerate the transportation of active oxygen species.

XPS spectra were further collected to analyze the detailed surface information of the catalysts. Ce $3d_{3/2}$ and Ce $3d_{5/2}$ display two main signals of binding energies at about 901 and 883 eV in Fig. 8(B). Four additional satellite peaks at ca. 917.1, 907.8, 898.5, and 889.2 eV are related to Ce⁴⁺ species, while those peaks located at 902.6, 898.8, 884.4, and 880.7 eV are characteristic of Ce³⁺ species [40]. As listed in Table 3, an increased content of Ce³⁺ after doping with WO₃ was found. For the charge balance, more oxygen vacancies will be produced in the HM-CeCuW and CP-CeCuW samples, which is further confirmed with the O 2p spectra. Three fitted peaks centered at 529.3, 530.3, and 531.7 eV are displayed in the spectra of O 2p in Fig. 8(C), correspond to lattice oxygen (O²⁻ marked as O_α), chemisorbed oxygen species (O²⁻, O⁻, and O₂²⁻ marked as O_β), and adsorbed molecular water (marked as O_γ), respectively. It was found that the O_β:O_α peak area ratio of HM-CeCuW was the highest among the four catalysts, verifying its largest number of

oxygen vacancies. Generally, more chemisorbed oxygen species are favorable for deep catalytic oxidation [41,42].

Regarding the Cu 2p spectra in Fig. 8(D), the peaks at 933.5 and 934.7 eV are related to Cu 2p_{3/2}, while the ones centered at 953.0 and 954.2 eV corresponded to Cu 2p_{1/2}. The two main peaks of CuO are accompanied with two satellite peaks at about 9 eV higher binding energies. For HM-CeCu and HM-CeCuW, the relative intensity of the satellite peaks with respect to the main peaks is almost 0.55 (the value for pure CuO is 0.55) [43]. The values are calculated to be 0.25 and 0.20 for CP-CeCu and CP-CeCuW, respectively. Hence, the Cu elements present in HM-CeCu and HM-CeCuW should be dominated by the CuO phase, while there exists some lower valence (<+2) of Cu species in CP-CeCu and CP-CeCuW. Besides, the presence of W⁶⁺ is well confirmed by the spectra of W 4f (Fig. 8(E)). The doping of W⁶⁺ results in an increase of Ce³⁺, and, hence, oxygen vacancies are induced. Meanwhile, as seen in Table 3, relatively higher surface content of Cu and W atoms are detected in HM-CeCuW when compared to CP-CeCuW, indicating the ammonium tungstate assisted hydrothermal method indeed favors the surface enrichment of W and the exposure of more active Cu species.

Table 3
Physico-chemical properties of catalysts.

Sample	S_{BET} (m ² /g)	Pore size (nm)	Crystal size of Cu (nm)	Ce ³⁺ :Ce ⁴⁺	O _β :O _α	Surface atomic concentration (%)		
						Ce	Cu	W
HM-CeCu	11	12.5	43.5	0.25	0.10	60	40	—
HM-CeCuW	31	12.9	11.9	0.37	0.34	50	44	6
CP-CeCu	86	8.6	87.7	0.28	0.08	68	32	—
CP-CeCuW	58	7.4	75.8	0.31	0.21	63	33	4

4. Conclusions

In summary, uniform microspheres of Ce-Cu-W-O catalysts were skillfully fabricated utilizing the solubility of ammonium tungstate in a special hydrothermal condition. The obtained catalysts were endowed with enhanced acidity, deduced from NH_3 -TPD, because of enriched surface WO_3 species. XRD analysis showed that W doping in HW-CeCu can restrict the growth of CuO nanoparticles, resulting in a promotion in reductivity, as confirmed in H_2 -TPR. Moreover, surface WO_3 in HW-CeCuW induced more Ce^{3+} and chemisorbed oxygen species, which are helpful for CVOC oxidation. In comparison, CP-CeCuW had the largest number of acid sites but showed weaker VC degradation activity than HW-CeCuW. This was due to its reduced reducibility after W doping, demonstrating reducibility and acidity are both important keys for VC oxidation. As a result, HM-CeCuW exhibited superior performance of VC oxidation, good stability, and high HCl selectivity. This work can provide new insights for designing advanced catalysts to eliminate CVOC emissions.

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Graphical Abstract

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Novel synthetic route to Ce-Cu-W-O microspheres for efficient catalytic oxidation of vinyl chloride emissions

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The solubility of ammonium tungstate in the hydrothermal condition was utilized to synthesize uniform microspheres of Ce-Cu-W-O oxides with both enhanced acidity and reducibility, which show excellent performance in the catalytic oxidation of vinyl chloride.

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用于氯乙烯废气高效催化氧化的Ce-Cu-W-O微球的新颖合成

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摘要: 含氯挥发性有机物(CVOC)氯乙烯(VC)出现在工业生产聚氯乙烯(PVC)的尾气中, 其具有高毒性和环境稳定性, 若直接排放到大气中, 会引起环境污染和威胁人类健康, 因此有效的去除CVOC至关重要。在众多处理技术, 催化氧化法具有反应温度低、能耗少、避免二次污染等优点, 因而备受关注。用于CVOC催化氧化的催化剂包含贵金属和非贵金属催化剂, 后者因为具有较低的成本和较好的抗氯中毒能力而广受研究。CVOC氧化催化剂通常需要具备酸性位和氧化还原位, 酸性位用来吸附活化CVOC分子, 而氧化还原位对应深度氧化能力。过渡金属氧化物CeO₂具有良好的储氧能力和氧化还原性而被作为催化材料应用于CVOC的催化氧化, 但深度氧化能力不佳。研究发现, 复合Cu氧化物可以提高CeO₂的氧化还原性, 继而提升催化剂对CVOC的氧化能力, 但酸性不足仍然限制了氯乙烯低温完全氧化的能力。为此, 可以尝试在Ce-Cu复合氧化物中引入氧化钨来提高催化剂的酸性, 但往往削弱了催化剂的氧化还原性, 且酸性位大多分布在催化剂体相中, 无法充分发挥其对VC分子的吸附活化。基于此, 本文利用钨酸铵随水热时间延长而逐渐溶解并扩散W离子的这一特性, 通过一步水热法设计合成了表面富集W物种和高分散精细Cu物种的Ce-Cu-W-O微球, 其相对于Ce-Cu-O催化剂具有同时更好的酸性和氧化还原性, 从而表现出对VC优异的深度氧化能力和热稳定性。

通过扫描电子显微镜, X射线能谱和X射线衍射分析, 我们解析了Ce-Cu-W-O微球上不同元素组分在水热过程中的生长阶段和物相状态。NH₃程序升温脱附分析验证了W物种的添加将提高Ce-Cu氧化物的酸性。H₂程序升温还原分析表明, 共沉淀方式引入W会降低Ce-Cu氧化物的氧化还原性, 而水热一步法制备Ce-Cu-W-O微球的氧化还原性却得到了改善, 归因于细小晶粒尺寸CuO物种的生成。此外, 拉曼光谱和XPS分析表明, HW-CeCuW催化剂具有更多的氧空位, 有利于活性氧物种的迁移。因此, Ce-Cu-W-O微球表现出优异的低温氧化活性(250 °C时的反应速率为 2.01×10^{-7} mol/(g_{cat}·s))和较高的HCl选择性。同时, Ce-Cu-W-O微球经三次循环测试后性能仅略微下降, 且在300 °C下进行72 h的耐久性实验中保持稳定的VC转化率和矿化率, 表明其良好的热稳定性。本合成策略可以为高效的CVOC催化氧化的金属氧化物催化剂的设计和合成提供一些新思路。

关键词: 氯乙烯催化氧化; Ce-Cu-W-O微球; 钨酸铵溶解性; 丰富表面WO₃; 精细CuO纳米颗粒

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