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Chlorine-Resistant Hollow Nanosphere-Like VO_x/CeO_2 Catalysts for Highly Selective and Stable Destruction of 1,2-Dichloroethane: Byproduct Inhibition and Reaction Mechanism

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Abstract: Developing economical and robust catalysts for the highly selective and stable destruction of chlorinated volatile organic compounds (CVOCs) is a great challenge. Here, hollow nanosphere-like VO_x/CeO_2 catalysts with different V/Ce molar ratios were fabricated and adopted for the destruction of 1,2-dichloroethane (1,2-DCE). The $\text{V}_{0.05}\text{Ce}$ catalyst possessed superior catalytic activity, reaction selectivity, and chlorine resistance owing to a large number of oxygen vacancies, excellent low-temperature redox ability, and chemically adsorbed oxygen (O^- and O_2^-) species mobility. Typical chlorinated byproducts (CHCl_3 , CCl_4 , C_2HCl_3 , and $\text{C}_2\text{H}_3\text{Cl}_3$) derived from the cleavage of C–Cl and C–C bonds of 1,2-DCE were detected, which could be effectively inhibited by the abundant acid sites and the strong interactions of VO_x species with CeO_2 . The presence of water vapor benefited the activation and deep destruction of 1,2-DCE over $\text{V}_{0.05}\text{Ce}$ owing to the efficient removal of Cl species from the catalyst surface.

Keywords: catalytic destruction; 1,2-dichloroethane; VO_x/CeO_2 ; chlorinated byproduct inhibition; reaction mechanism

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1. Introduction

Chlorinated volatile organic compounds (CVOCs) mainly originate from industrial processes and result in great hazards to public health and the natural environment because of their long durability, poor reactivity, and high toxicity [1–3]. So far, several methods including absorption, photocatalytic degradation, catalytic oxidation, and biological processes have been used for CVOC elimination [4]. Among them, catalytic oxidation has been identified as the most efficient treatment measure due to its significant energy saving, adjustable reaction selectivity, low operation temperature, and green environment effect [5,6]. Up to now, various catalysts including transition metal oxides, zeolites/modified zeolites, and supported noble metals have been studied for CVOC destruction. Supported noble-metal catalysts exhibit outstanding catalytic performance, whereas their widespread application is greatly limited by their susceptibility to chlorine poisoning, the formation of chlorinated byproducts, and their high cost [7,8]. Although zeolites/modified zeolites exhibit good catalytic performance, they more easily suffer deactivation due to chlorine poisoning and coke deposition during the oxidation process [9,10].

Comparatively, transition metal oxides (e.g., Cr_2O_3 , MnO_x , and V_2O_5) are considered as a category of desired candidates to destroy CVOCs owing to their considerable

catalytic performance, high availability, and low cost [6,11–13]. For example, VO_x catalysts are usually used for CVOC destruction due to their excellent resistance to chlorine poisoning [13,14]. Recently, CeO_2 catalysts attracted much attention for CVOC destruction attributed to their higher oxygen mobility, superior redox ability, and abundant oxygen vacancies. However, CeO_2 catalysts are easily deactivated because of the strong adsorption of Cl species onto their active sites. Generally, the introduction of transition metal oxides is advantageous for promoting activity and stability. Dai et al. [15] presented that a 6 wt.% VO_x/CeO_2 catalyst displayed superior catalytic activity for 1,2-dichloroethane (1,2-DCE) degradation owing to the strong interaction of VO_x species with CeO_2 and the high valence of VO_x . It was observed that the stability of VO_x/CeO_2 materials was significantly improved, attributed to the VO_x species preventing Cl species from exchanging the surface lattice oxygen of CeO_2 during chlorobenzene destruction [16]. Although VO_x/CeO_2 catalysts have made certain progress in CVOC destruction, there are many issues that should be further solved and clarified; for instance, the role of VO_x and/or the synergistic effect of VO_x/CeO_2 in the production of chlorinated byproducts requires an in-depth study, as well as the effect of water vapor on catalytic performance and chlorinated byproduct distributions over VO_x/CeO_2 catalysts. It was reported that CeO_2 material with a hollow nanosphere structure ($\text{CeO}_2\text{-HS}$) had abundant oxygen vacancies and a large surface area, which is favorable for VOC oxidation [17]. Meanwhile, $\text{CeO}_2\text{-HS}$ with high stability and water resistance is a potential carrier for fabricating effective CVOC oxidation materials.

Herein, hollow nanosphere-like VO_x/CeO_2 catalysts with well-dispersed VO_x species, abundant surface acid sites, and outstanding low-temperature reducibility were fabricated via a simple wetness impregnation process. The structural properties, reducibility, oxygen mobility, and acidity of prepared materials were deeply analyzed using various techniques such as field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), the hydrogen temperature programmed reduction ($\text{H}_2\text{-TPR}$), X-ray photoelectron spectroscopy (XPS), the temperature programmed desorption of O_2 ($\text{O}_2\text{-TPD}$) and the temperature programmed desorption of NH_3 ($\text{NH}_3\text{-TPD}$). Catalytic activity and stability, yields of CO and CO_2 , and the distribution of chlorinated byproducts over prepared materials were studied in detail. In particular, the influence of water vapor on catalytic performance and the vital factors inhibiting the generation of chlorinated byproducts were explored. Accordingly, the destruction mechanism of 1,2-DCE over VO_x/CeO_2 samples was further proposed.

2. Materials and Methods

2.1. Catalyst Preparation

Hollow nanosphere-like CeO_2 was prepared using a hydrothermal route [18]. Specifically, 5.0 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 5 mL of CH_3COOH (36 wt.%) were added into 150 mL of a mixed solution (ethylene glycol (100 mL) and deionized water (50 mL)) under vigorous stirring for 0.5 h. After that, 4.0 g of polyvinyl pyrrolidone (PVP; K-30) was added, with continued stirring at 60 °C for 1 h. The solution was then placed into a 200 mL Teflon-lined stainless-steel autoclave and kept at 180 °C for 6 h. Finally, the precursor was centrifuged, washed, dried, and calcined at 500 °C for 4 h in air.

Hollow nanosphere-like VO_x/CeO_2 materials were prepared via a wetness impregnation approach. Typically, 3.0 g of the above-prepared CeO_2 was dispersed into 150 mL of deionized water, and an appropriate amount of NH_4VO_3 with the molar ratio of $n\text{NH}_4\text{VO}_3:n\text{CeO}_2 = 0.025:1, 0.05:1, 0.1:1, \text{ or } 0.2:1$ was then mixed in the above solution. Subsequently, the corresponding molar amount of oxalic acid with the molar ratio of $n\text{NH}_4\text{VO}_3:\text{noxic acid} = 1:2$ was added to the suspension of CeO_2 . After that, the solution was vigorously stirred at 80 °C until excess deionized water was completely evaporated. The final products were treated under the same conditions as for CeO_2 preparation. The obtained materials were designated as $\text{V}_{0.025}\text{Ce}$, $\text{V}_{0.05}\text{Ce}$, $\text{V}_{0.1}\text{Ce}$, and $\text{V}_{0.2}\text{Ce}$, respectively.

In comparison, VO_x was also prepared using a hydrothermal method [19]. The prepared powder was also treated as in the CeO_2 preparation process to obtain the bulk

VO_x. Additionally, commercial CeO₂ (Aladdin Reagent Co., Ltd., Shanghai, China, 99.5%) named CeO₂-C was also investigated for 1,2-DCE oxidation.

2.2. Catalyst Characterizations

The prepared materials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectra (FT-IR), low-temperature N₂ adsorption/desorption, FE-SEM, HR-TEM, XPS, H₂-TPR, O₂-TPD, NH₃-TPD, FT-IR spectra of NH₃ adsorption (NH₃-IR), and in situ diffuse reflectance infrared spectroscopy (DRIFTS). The detailed information can be found in the Supplementary Materials.

2.3. Catalytic Activity

The 1,2-DCE destruction experiments were employed in a continuous-flow fixed-bed quartz tube reactor with 10.0 mm inner diameter. Typically, the prepared catalyst (500 mg; 40–60 mesh) was loaded into the isothermal region of the tube reactor. The reactant mixture containing 1000 ppm of 1,2-DCE, 79% N₂, and 21% O₂, with a total flow rate of 250 mL·min^{−1} (gas hourly space velocity (GHSV) = 30,000 mL·g^{−1}·h^{−1}) was obtained through the reactor. The concentrations of 1,2-DCE, chlorinated byproducts, and CO_x (CO and CO₂) were measured using an online gas chromatograph (GC9890, China) with Electron Capture Detector (ECD). Furthermore, an online Cl₂ and HCl detector (PN-2000, China) was used to analyze the concentrations of Cl₂ and HCl.

The 1,2-DCE conversion ($X_{1,2\text{-DCE}}$) was calculated using Equation (1).

$$X_{1,2\text{-DCE}} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\%, \quad (1)$$

where C_{in} and C_{out} refer to the inlet and outlet 1,2-DCE concentrations, respectively.

The CO and CO₂ yields (Y_{CO} and Y_{CO_2}) were calculated using Equations (2) and (3), respectively.

$$Y_{\text{CO}} = \frac{C_{\text{CO}}}{2C_{\text{in}}} \times 100\%, \quad (2)$$

$$Y_{\text{CO}_2} = \frac{C_{\text{CO}_2}}{2C_{\text{in}}} \times 100\%, \quad (3)$$

where C_{CO} and C_{CO_2} refer to the outlet concentrations of CO and CO₂, respectively.

The stability of the prepared catalysts was evaluated at different temperatures corresponding to 90% conversion of 1,2-DCE under the same conditions as the activity experiments. Moreover, the stability of the highest-activity V_{0.05}Ce sample for 1,2-DCE oxidation was studied in the absence and presence of water vapor. Different concentrations of water vapor (1, 2, and 5 vol.%) were injected into the reactant mixture containing 1000 ppm of 1,2-DCE using an automatic sample injector.

3. Results

3.1. Structural and Textural Properties

Figure 1a and Figure S1 (Supplementary Materials) exhibit the XRD patterns of prepared catalysts. The peaks located at 28.4°, 33.1°, 47.4°, 56.3°, 59.1°, 69.6°, 76.6°, and 79.2° were attributed to the (111), (200), (220), (311), (222), (400), (331), and (420) crystal planes of CeO₂, respectively [20]. The characteristic peaks of VO_x (V₂O₅) were located at 15.3°, 20.2°, 21.7°, 26.1°, 31.0°, 32.4°, 34.3°, and 47.4° [21]. Notably, no characteristic peaks corresponding to VO_x and CeVO₄ species (2θ = 24.0° and 32.5°) could be detected over VO_x/CeO₂ catalysts, suggesting that VO_x species were highly dispersed on the surface or in the form of a solid solution [15,22]. The position of the main peak of CeO₂ (ca. 28.4°) was well maintained over VO_x/CeO₂ materials, suggesting that VO_x neither altered the CeO₂ crystallization nor was incorporated into the CeO₂ crystalline phase, forming a solid solution [15,23]. Hence, VO_x species existed in a highly dispersed form.

Figure 1. (a) X-ray diffraction (XRD) profiles and (b) Fourier transform infrared spectra (FT-IR) of prepared catalysts.

As shown in Figure 1b, the broad IR peaks over all catalysts between 3500 and 3000 cm^{-1} corresponded to the stretching vibration of surface hydroxyl groups, while the peaks presented at 1622 cm^{-1} were indexed as C=O stretching vibration [24]. For CeO_2 , the peaks located at wavenumbers lower than 1000 cm^{-1} were associated with the vibration of Ce–O [25]. For VO_x , the peaks located in the 1100–400 cm^{-1} region were related to the V–O stretching vibration [26]. The peaks centered at 1045 and 841 cm^{-1} were consistent with the symmetric stretching vibration of $\text{V}^{5+}=\text{O}$ and stretching vibration of $\text{O}-(\text{V})_3$, respectively. It can be observed that $\text{V}^{5+}=\text{O}$ vibration located at 1045 cm^{-1} was detected over VO_x and VO_x/CeO_2 catalysts [26]. The two peaks over VO_x/CeO_2 catalysts at 715 and 841 cm^{-1} could be regarded as the V–O–Ce modes [27]. In addition, the symmetric and antisymmetric stretching vibration of V–O–V could be detected in the 700–400 cm^{-1} range over VO_x and VO_x/CeO_2 catalysts [26].

FE-SEM images of prepared catalysts are shown in Figure 2a–x. CeO_2 exhibited a regular nanosphere-like morphology with different diameters (ca. 245–600 nm), as displayed in Figure 2a,b. The $\text{V}_{0.05}\text{Ce}$ catalyst was made up of nanospheres with a diameter of ca. 100–200 nm (Figure 2e,f). Compared with the $\text{V}_{0.05}\text{Ce}$ catalyst, $\text{V}_{0.025}\text{Ce}$ (Figure 2c,d), $\text{V}_{0.1}\text{Ce}$ (Figure 2g,h) and $\text{V}_{0.2}\text{Ce}$ catalysts (Figure 2i,j) consisted of larger nanosphere-like particles with a diameter of ca. 300–400 nm. Moreover, VO_x showed an irregular nanosphere-like morphology with size varying from ca. 200 to 300 nm (Figure 2k,l). Figure 2m–x and Figure S2 (Supplementary Materials) exhibit the transmission electron microscope (TEM) and high-angle annular dark-field imaging in scanning transmission electron microscopy (HAADF-STEM) images of prepared catalysts. It was revealed that CeO_2 and VO_x/CeO_2 catalysts possessed a well-defined hollow nanosphere-like structure with diameter in the range of ca. 200–400 nm, in agreement with the FE-SEM results. The results exhibited that VO_x species were highly dispersed and did not change CeO_2 morphology [28]. VO_x had an irregular nanosphere-like morphology with a lattice spacing of 0.34 nm, ascribed to the (101) plane of V_2O_5 (Figure 2w,x) [29]. The measured lattice distances of 0.31, 0.27, and 0.19 nm were ascribed to the (111), (200), and (220) lattice planes of CeO_2 nanospheres (JCPDS #34-0394), respectively (Figure 2n). Figure 2p,r,t and Figure S2 (Supplementary Materials) show that $\text{V}_{0.025}\text{Ce}$, $\text{V}_{0.05}\text{Ce}$, $\text{V}_{0.1}\text{Ce}$, and CeO_2 -C catalysts possessed the (200) and (111) lattice planes of CeO_2 with lattice spacings of 0.27 and 0.31 nm, respectively. For $\text{V}_{0.2}\text{Ce}$, the lattice spacings of 0.27 and 0.19 nm were associated with the (200) and (220) crystal planes of CeO_2 , respectively (Figure 2v). No VO_x species on the VO_x/CeO_2 catalysts could be detected in HAADF-STEM images (Figure 2p,r,t,v), which could be attributed to the rough surface of CeO_2 or the generation of VO_x films from the layer structure [15].

Figure 2. Field emission scanning electron microscopy (FE–SEM) images of (a,b) CeO_2 , (c,d) $\text{V}_{0.025}\text{Ce}$, (e,f) $\text{V}_{0.05}\text{Ce}$, (g,h) $\text{V}_{0.1}\text{Ce}$, (i,j) $\text{V}_{0.2}\text{Ce}$, and (k,l) VO_x ; high-resolution transmission electron microscopy (HR–TEM) patterns of (m,n) CeO_2 , (o,p) $\text{V}_{0.025}\text{Ce}$, (q,r) $\text{V}_{0.05}\text{Ce}$, (s,t) $\text{V}_{0.1}\text{Ce}$, (u,v) $\text{V}_{0.2}\text{Ce}$, and (w,x) VO_x .

N_2 adsorption/desorption isotherms of the prepared materials are presented in Figure 3. CeO_2 and VO_x/CeO_2 catalysts showed a type II isotherm curve with H3-type hysteresis loops at the relative pressure (P/P_0) range of 0.7–1.0 (Figure 3a), indicating that meso- and macropore structures co-existed in CeO_2 and VO_x/CeO_2 catalysts [30,31]. VO_x exhibited a type III isotherm curve with H3-type hysteresis loops ($P/P_0 = 0.9$ –1.0), illustrating that the presence of textural pores facilitated the filling of interparticle spaces. It was demonstrated that the pore size distribution of prepared catalysts was centered at approximately 25.4, 11.7, 19.4, 37.6, 27.0, and 17.4 nm, respectively (Figure 3b), indicating that all catalysts possessed a large number of mesopores. The pore size distribution of materials in the 100–500 nm region could be attributed to the existence of a macroporous structure. The specific surface area, average pore diameter, and pore volume of materials are documented in Table 1, and the average pore diameter followed the order of VO_x (63.1 nm) > $\text{V}_{0.1}\text{Ce}$ (30.1 nm) > $\text{V}_{0.025}\text{Ce}$ (18.0 nm) > $\text{V}_{0.2}\text{Ce}$ (14.8 nm) > CeO_2 (13.2 nm) > $\text{V}_{0.05}\text{Ce}$ (10.7 nm). The specific surface area of CeO_2 and VO_x/CeO_2 was much higher than that of VO_x , which obeyed the sequence of CeO_2 ($110.9 \text{ m}^2 \cdot \text{g}^{-1}$) > $\text{V}_{0.025}\text{Ce}$ ($101.0 \text{ m}^2 \cdot \text{g}^{-1}$) > $\text{V}_{0.05}\text{Ce}$ ($98.6 \text{ m}^2 \cdot \text{g}^{-1}$) > $\text{V}_{0.1}\text{Ce}$ ($93.4 \text{ m}^2 \cdot \text{g}^{-1}$) > $\text{V}_{0.2}\text{Ce}$ ($76.1 \text{ m}^2 \cdot \text{g}^{-1}$) >> VO_x ($11.3 \text{ m}^2 \cdot \text{g}^{-1}$). It was revealed that the specific surface area of VO_x/CeO_2 catalysts decreased along with the increase in VO_x loading because of the partial blockage of CeO_2 pores by VO_x species [28].

Figure 3. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of prepared catalysts.

Table 1. Textural properties and catalytic performance of prepared catalysts.

Sample	S_{BET}^a ($\text{m}^2 \cdot \text{g}^{-1}$)	V_t^b ($\times 10^{-2}$, $\text{cm}^3 \cdot \text{g}^{-1}$)	D_p^c (nm)	T_{50}^d ($^{\circ}\text{C}$)	T_{90}^d ($^{\circ}\text{C}$)
CeO ₂	110.9	36.54	13.2	328	381
V _{0.025} Ce	101.0	45.46	18.0	299	367
V _{0.05} Ce	98.6	26.43	10.7	281	347
V _{0.1} Ce	93.4	30.46	30.1	294	356
V _{0.2} Ce	76.1	28.18	14.8	307	413
VO _x	11.3	17.92	63.1	/	/

^a Specific surface area obtained at $P/P_0 = 0.05\text{--}0.30$ by the Brunauer–Emmett–Teller (BET) method; ^b total pore volume estimated at $P/P_0 = 0.99$; ^c pore diameter calculated from the N₂ desorption branch by the Barrett–Joyner–Halenda (BJH) method; ^d temperatures at which 50% and 90% conversion of 1,2-dichloroethane (1,2-DCE) occurred.

3.2. Surface Composition and Element Status

The surface elemental composition and oxidation status of prepared materials were characterized through XPS, as illustrated in Figure 4 and Table 2. The C 1s, O 1s, V 2p, and Ce 3d peaks of prepared materials could be detected, as shown in Figure 4a. As shown in Figure 4b, O 1s XPS spectra were classified into three sub-peaks centered at 529.3–529.9, 531.5–531.9, and 533.0–533.4 eV, which were attributed to lattice oxygen (O_{α} ; O^{2-}), surface oxygen species adsorbed on oxygen vacancies (O_{β} ; O_2^{2-} , O^- , OH^- , and CO_3^{2-}), and carbonates and/or water (O_{γ}), respectively [32,33]. The $O_{\beta}/(O_{\alpha} + O_{\beta})$ ratios of prepared catalysts followed the sequence of V_{0.05}Ce (0.61) > V_{0.1}Ce (0.57) > V_{0.025}Ce (0.54) > CeO₂ (0.48) > V_{0.2}Ce (0.46) > VO_x (0.45) (Table 2), suggesting that the V_{0.05}Ce catalyst possessed the largest number of surface oxygen species, facilitating the destruction of 1,2-DCE [5]. Figure 4c shows the V 2p XPS spectra of VO_x and VO_x/CeO₂ catalysts. Only V⁵⁺ species could be detected over VO_x, corresponding to the presence of the V₂O₅ phase. The peaks at 517.1–517.4 and 515.0–515.4 eV represented V⁵⁺ and V⁴⁺, respectively, suggesting that V⁵⁺ and V⁴⁺ species co-existed on VO_x/CeO₂ catalysts [34]. Moreover, the peak-fitting results demonstrated that VO_x/CeO₂ catalysts were mainly composed of V⁵⁺ species corresponding to the V₂O₅ phase [21,34]. As shown in Table 2, the ratios of V⁵⁺/(V⁴⁺ + V⁵⁺) for V_{0.025}Ce, V_{0.05}Ce, V_{0.1}Ce, and V_{0.2}Ce catalysts were 0.84, 0.87, 0.85, and 0.83, respectively, indicating that the V_{0.05}Ce material possessed high ratios of V⁵⁺/(V⁴⁺ + V⁵⁺), favorable for 1,2-DCE oxidation. The Ce 3d XPS spectra were split into eight sub-peaks, as depicted in Figure 4d. Six peaks of Ce 3d labeled by V, V'', V''', U, U'', and U''' were assigned to Ce⁴⁺ species and the other two peaks labeled by U' and V' belonged to Ce³⁺ species [34]. The Ce³⁺/(Ce³⁺ + Ce⁴⁺) ratios of prepared catalysts were calculated according to the corresponding peak areas, as documented in Table 2. Generally,

surface oxygen vacancies were formed by the removal of lattice oxygen species (O_α) in CeO_2 , causing the formation of Ce^{3+} species ($Ce^{4+} + e^- \rightarrow Ce^{3+} + \diamond$) [35]. According to Table 2, $Ce^{3+}/(Ce^{3+} + Ce^{4+})$ ratios of prepared materials followed the order of $V_{0.05}Ce$ (0.19) > $V_{0.1}Ce$ (0.18) > $V_{0.025}Ce$ (0.17) > CeO_2 (0.15) > $V_{0.2}Ce$ (0.13), suggesting that $V_{0.05}Ce$ owned the largest amount of Ce^{3+} species. It was reported that a large amount of Ce^{3+} species contributes to the formation of oxygen vacancies, which can effectively accelerate the mobility of active oxygen species and consequently promote the catalytic activity [35]. This result also suggested that VO_x species interaction with CeO_2 was strongest over $V_{0.05}Ce$, leading to the formation of more low-valence Ce^{3+} species [28].

Figure 4. X-ray photoelectron spectroscopy (XPS) spectra of prepared catalysts: (a) C 1s, (b) O 1s, (c) V 2p, and (d) Ce 3d.

Table 2. XPS results of prepared catalysts.

Sample	Binding Energy (eV)						Molar Ratio	
	V^{4+}	V^{5+}	O_α ^a	O_β ^b	O_γ ^c	$O_\beta/(O_\alpha + O_\beta)$	$V^{5+}/(V^{5+} + V^{4+})$	$Ce^{3+}/(Ce^{3+} + Ce^{4+})$
CeO_2	/	/	529.5	531.5	533.2	0.48	/	0.15
$V_{0.025}Ce$	515.2	517.1	529.3	531.7	533.0	0.54	0.84	0.17
$V_{0.05}Ce$	515.4	517.2	529.5	531.6	533.1	0.61	0.87	0.19
$V_{0.1}Ce$	515.0	517.2	529.4	531.9	533.4	0.57	0.85	0.18
$V_{0.2}Ce$	515.4	517.4	529.9	531.8	533.3	0.46	0.83	0.13
VO_x	/	517.2	529.6	531.9	533.3	0.45	/	/

^a Lattice oxygen species; ^b surface oxygen species; ^c adsorbed oxygen species from hydroxyl and adsorbed water on the surface.

3.3. Reducibility and Oxygen Species Mobility

An H₂-TPR experiment was employed to test the redox properties of all samples, as depicted in Figure 5a. For CeO₂, the reduction peaks presented at ca. 524 and 785 °C were respectively associated with the reduction of surface Ce⁴⁺ to Ce³⁺ and bulk CeO₂ [28]. The introduction of VO_x could effectively enhance the redox capacity of CeO₂. For VO_x/CeO₂ catalysts, the reduction peaks located at 518, 500, 507, and 526 °C were indexed to the reduction of VO_x species (V⁵⁺ → V⁴⁺), while the peaks at 436, 454, 466, and 492 °C were indexed to the reduction of surface CeO₂ (Ce⁴⁺ → Ce³⁺) [22,28], indicating the co-existence of Ce⁴⁺/Ce³⁺ and V⁵⁺/V⁴⁺ species, in accordance with the XPS results (Figure 4). It is illustrated that the reduction temperature of VO_x species in VO_x/CeO₂ (except V_{0.025}Ce) catalysts apparently shifted to higher temperatures along with the increase in VO_x loading due to the CeO₂ interaction with VO_x species affecting the redox performance of surface CeO₂ [22]. The total H₂ consumption of prepared materials below 600 °C followed the order of V_{0.05}Ce (9.86 mmol·g^{−1}) > V_{0.1}Ce (9.53 mmol·g^{−1}) > V_{0.025}Ce (8.64 mmol·g^{−1}) > CeO₂ (8.02 mmol·g^{−1}) > V_{0.2}Ce (7.63 mmol·g^{−1}), suggesting that V_{0.05}Ce possessed superior reducibility (Table 3). Additionally, the initial H₂ consumption (less than 25% H₂ consumption for the first reduction peak) rate was also employed to evaluate the low-temperature reducibility of all catalysts [24]. Figure 5b shows that the initial H₂ consumption rates of the catalysts followed the sequence of V_{0.05}Ce > V_{0.1}Ce > V_{0.025}Ce > CeO₂ > V_{0.2}Ce, suggesting that V_{0.05}Ce had superior low-temperature reducibility.

Figure 5. (a) Hydrogen temperature programmed reduction (H₂-TPR) and (b) the initial H₂ consumption rate of prepared catalysts.

Table 3. H₂-TPR, O₂-TPD, and NH₃-TPD results of prepared catalysts.

Sample	H ₂ Consumption (mmol·g ^{−1})	O ₂ Desorption Peaks			NH ₃ Desorption Peaks
	<i>P</i> ^a	<i>P</i> ₁ ^b	<i>P</i> ₂ ^c	<i>P</i> ₃ ^d	<i>P</i> ^e
CeO ₂	8.02	25,200	7190	5029	231.78
V _{0.025} Ce	8.64	40,000	9423	11,700	250.55
V _{0.05} Ce	9.86	30,700	13,700	26,900	257.03
V _{0.1} Ce	9.53	27,800	12,256	56,600	244.76
V _{0.2} Ce	7.63	8536	2551	59,100	223.09
VO _x	/	/	/	26,700	83.87

^a Hydrogen consumption at 100–600 °C; ^b areas of physically adsorbed oxygen species; ^c chemically adsorbed oxygen (O[−] and O₂[−]) species; ^d weak surface lattice oxygen (O^{2−}) species; ^e total area of NH₃ desorption peaks.

The O₂-TPD results of prepared materials are displayed in Figure 6. Generally, the peaks located at <250, 250–550, and 550–750 °C could be regarded as the physically adsorbed oxygen species, chemically adsorbed oxygen (O[−] and O₂[−]) species, and weak

surface lattice oxygen (O^{2-}) (bulk lattice oxygen at above 750 °C), respectively [36,37]. For CeO_2 and VO_x/CeO_2 catalysts, the desorption peaks located at 169, 160, 187, 193, and 176 °C were assigned to the physically adsorbed oxygen (O^- and O_2^-) species. The desorption peaks in the region of 250–550 °C corresponded to the chemically adsorbed oxygen species. Additionally, the desorption peaks located at 642, 747, 706, 644, and 565 °C could be associated with the weak surface lattice oxygen (O^{2-}) [16,38]. Generally, the lattice oxygen diffused from bulk to surface, which further promoted the reduction of V^{5+} to V^{4+} and Ce^{4+} to Ce^{3+} [38]. For the VO_x catalyst, the desorption peaks presented at 629 and 684 °C were consistent with the weak surface lattice oxygen (O^{2-}). As displayed in Table 3, the desorption amount of chemically adsorbed oxygen (O^- and O_2^-) species followed the sequence of $V_{0.05}Ce > V_{0.1}Ce > V_{0.025}Ce > CeO_2 > V_{0.2}Ce$, suggesting that $V_{0.05}Ce$ possessed excellent chemically adsorbed oxygen (O^- and O_2^-) species mobility, favorable for 1,2-DCE oxidation.

Figure 6. Temperature programmed desorption of O_2 (O_2 -TPD) profiles of prepared catalysts.

3.4. Surface Acidity

The acidity properties of the prepared catalysts were investigated through NH_3 -TPD, as displayed in Figure 7a. Generally, the NH_3 desorption spectra of prepared catalysts were divided into three peaks corresponding to weak acidity (<200 °C), moderate acidity (200–400 °C), and strong acidity (>400 °C) [24]. CeO_2 displayed two peaks presented at 198 and 365 °C, which were related to the weak and moderate acid sites, respectively. The broad peaks over $V_{0.05}Ce$ (232 °C) and $V_{0.1}Ce$ (246 °C) catalysts were attributed to the moderate acid sites. Similarly, $V_{0.025}Ce$, $V_{0.2}Ce$, and VO_x catalysts also exhibited wide peaks at 160, 187, and 157 °C, which corresponded to the weak acid sites. The total NH_3 desorption amount of the prepared catalysts followed the order of $V_{0.05}Ce > V_{0.1}Ce > V_{0.025}Ce > CeO_2 > V_{0.2}Ce \gg VO_x$ (Table 3), which revealed that the opportune introduction of VO_x could enhance the total acidity of CeO_2 . $V_{0.05}Ce$ possessed the largest number of acid sites, crucial for promoting the adsorption and activation of 1,2-DCE molecules [39].

Figure 7. (a) Temperature programmed desorption of NH_3 (NH_3 -TPD) and (b) FT-IR spectra of NH_3 adsorption (NH_3 -IR) profiles of prepared catalysts.

An NH_3 -IR analysis of prepared catalysts was further conducted to characterize the acid site types, as shown in Figure 7b. Generally, the bands in the regions of 1500–1400 and 1690–1660 cm^{-1} were associated with the symmetric and antisymmetric stretching vibrations of NH_4^+ species adsorbed on Brønsted acid (designed as B) sites [40,41]. The bands at 1300–1200 and 1600–1540 cm^{-1} were related to the symmetric and antisymmetric stretching vibration of NH_3 adsorbed on Lewis acid (designed as L) sites [30,40]. For CeO_2 , the band located at 1429 cm^{-1} was related to the B acid sites, and the bands centered at 1279 and 1551 cm^{-1} could be connected to the L acid sites. The bands at 1296, 1541, and 1599 cm^{-1} associated with L acid sites over $\text{V}_{0.025}\text{Ce}$ could be detected. For $\text{V}_{0.05}\text{Ce}$, the band located at 1437 cm^{-1} corresponded to the B acid sites, while the bands centered at 1541 and 1599 cm^{-1} corresponded to the L acid sites. Compared with CeO_2 , more B and L acid sites could be observed over $\text{V}_{0.05}\text{Ce}$. For $\text{V}_{0.1}\text{Ce}$ and $\text{V}_{0.2}\text{Ce}$, the bands at 1404, 1427, and 1672 cm^{-1} could be ascribed to the B acid sites. However, no L acid sites could be detected over $\text{V}_{0.1}\text{Ce}$ and $\text{V}_{0.2}\text{Ce}$ catalysts, indicating that more L acid sites were occupied with the increase in V loading [30]. The bands at 1404 and 1427 cm^{-1} over VO_x corresponded to the B acid sites.

4. Discussion

4.1. Catalytic Activity and Stability

All prepared materials were evaluated in 1,2-DCE destruction, as exhibited in Figure 8a. According to T_{90} (the temperature for 90% conversion of 1,2-DCE), the activity sequence of synthesized materials was in the order of $\text{V}_{0.05}\text{Ce}$ (347 °C) > $\text{V}_{0.1}\text{Ce}$ (356 °C) > $\text{V}_{0.025}\text{Ce}$ (367 °C) > CeO_2 (381 °C) > $\text{V}_{0.2}\text{Ce}$ (413 °C) > $\text{CeO}_2\text{-C}$ (> 450 °C) >> VO_x . The catalytic activity of $\text{CeO}_2\text{-C}$ was significantly lower than that of hollow nanosphere-like CeO_2 , indicating that the designed hollow nanosphere structure for CeO_2 had an advantage in 1,2-DCE degradation. Furthermore, it could be found that the activity of all catalysts increased slowly (<240 °C) and then enhanced rapidly with the increase in temperature as 1,2-DCE was firstly adsorbed at relatively low temperature and then activated with increasing temperature. Compared with CeO_2 , the activity of $\text{V}_{0.025}\text{Ce}$, $\text{V}_{0.05}\text{Ce}$, and $\text{V}_{0.1}\text{Ce}$ catalysts was obviously improved because the strong interaction of VO_x species with CeO_2 could promote the efficient removal of Cl species on the catalyst surface [16]. On the other hand, the catalytic activity of $\text{V}_{0.2}\text{Ce}$ was lower than that of CeO_2 , which was related to the excessive VO_x content covering some oxygen vacancies or active sites of CeO_2 and inhibiting the removal of Cl species [42]. According to the XPS results in Figure 4d, $\text{V}_{0.05}\text{Ce}$ possessed the highest amount of Ce^{3+} , indicating the presence of more oxygen vacancies in CeO_2 , which could be advantageous to improving the mobility of active oxygen species and further promoting the oxidation of 1,2-DCE. According to H_2 -TPR and O_2/NH_3 -TPD results (Figures 5–7), it was demonstrated that $\text{V}_{0.05}\text{Ce}$ possessed superior low-temperature

reducibility, excellent chemically adsorbed oxygen (O^- and O_2^-) species mobility, and a large number of acid sites, facilitating the adsorption and oxidation of 1,2-DCE. Moreover, the strong interaction of VO_x species with CeO_2 could also efficiently enhance the activity of $V_{0.05}Ce$.

Figure 8. (a) Catalytic activity, (b) CO yield, (c) CO_2 yield, and (d) stability of prepared catalysts for 1,2-DCE destruction.

The yields of CO and CO_2 as a function of temperature were analyzed in Figure 8b,c. It was revealed that the yields of CO and CO_2 over CeO_2 and CeO_2-C catalysts increased with increasing temperature; however, much different behaviors could be found over VO_x/CeO_2 . The yields of CO and CO_2 over CeO_2 only had a tiny gap and could reach approximately 50% at 450 °C, whereas the yields of CO (46%) and CO_2 (35%) over CeO_2-C were lower than that of hollow nanosphere-like CeO_2 . It could be found that the yield of CO significantly increased when VO_x species were loaded on the surface of CeO_2 . In addition, the yields of CO and CO_2 over $V_{0.025}Ce$, $V_{0.1}Ce$, and $V_{0.2}Ce$ catalysts increased with increasing temperature. However, the yield of CO over $V_{0.05}Ce$ catalyst initially increased and then decreased with increasing temperature, attributed to the further oxidation of CO (>360 °C). It was reported that the final product mainly containing carbon species is CO over VO_x/CeO_2 catalysts during 1,2-DCE destruction, and the high yield of CO is presumed to be connected to the surface lattice oxygen of VO_x [15].

Reaction stability is one of the most important indices to evaluate the application prospect of a catalyst. The stabilities of $V_{0.05}Ce$, CeO_2 , and VO_x were studied at approximately T_{90} temperatures, as shown in Figure 8d. The $V_{0.05}Ce$ catalyst possessed outstanding catalytic stability and resistance to chlorine poisoning, maintaining approximately 94% of 1,2-DCE conversion at 347 °C for 32 h. Similarly, the catalytic stability of CeO_2 was maintained at approximately 92% at 384 °C in 32 h. However, the conversion of 1,2-DCE over VO_x decreased distinctly from 93% to 83% in the first 27 h, which could be ascribed to the attack of Cl species, leading to the loss of active sites.

4.2. Chlorinated Intermediate Species Distribution and Proposed Reaction Mechanism

CO_2 , CO , HCl , and Cl_2 are the ideal products for CVOC destruction; however, chlorinated byproducts are usually inevitably formed. In this work, 1,1,2-trichloroethane ($\text{C}_2\text{H}_3\text{Cl}_3$), vinyl chloride ($\text{C}_2\text{H}_3\text{Cl}$), trichloroethylene (C_2HCl_3), dichloromethane (CH_2Cl_2), trichloromethane (CHCl_3), and perchloromethane (CCl_4) were observed during the oxidation of 1,2-DCE. CCl_4 , CHCl_3 , C_2HCl_3 , and $\text{C}_2\text{H}_3\text{Cl}_3$ as primary chlorinated byproducts collected at different reaction temperatures. Figure 9 presents the remarkable differences in the concentration of chlorinated byproducts detected over all catalysts. The concentrations of CCl_4 , CHCl_3 , C_2HCl_3 , and $\text{C}_2\text{H}_3\text{Cl}_3$ over VO_x/CeO_2 catalysts were obviously lower than those over CeO_2 and VO_x . Additionally, it was observed that the concentrations of chlorinated byproducts over CeO_2 and VO_x/CeO_2 catalysts firstly increased and then decreased with increasing test temperature ($>250^\circ\text{C}$). The appropriate introduction of VO_x species ($\text{V}_{0.025}\text{Ce}$, $\text{V}_{0.05}\text{Ce}$, and $\text{V}_{0.1}\text{Ce}$) in CeO_2 was advantageous for the catalytic activity of CeO_2 and remarkably inhibited the formation of chlorinated byproducts, ascribed to the strong interaction between VO_x species and CeO_2 and the superior removal ability of Cl species during 1,2-DCE oxidation [30,43].

Figure 9. Chlorinated byproducts distribution in 1,2-DCE destruction over prepared catalysts: (a) CHCl_3 , (b) CCl_4 , (c) C_2HCl_3 , and (d) $\text{C}_2\text{H}_3\text{Cl}_3$.

The reaction process of 1,2-DCE over prepared materials was deeply studied using an in situ DRIFTS experiment, as displayed in Figure 10. The broad bands presented at $3100\text{--}4000\text{ cm}^{-1}$ were indexed to the stretching vibrations of hydrogen-bonded OH [15,44]. Additionally, no bands corresponding to VO_x species were detected over VO_x/CeO_2 catalysts because of the highly dispersed VO_x species on the CeO_2 surface [44].

Figure 10. In situ diffuse reflectance infrared spectroscopy (DRIFTS) of 1,2-DCE catalytic oxidation: (a) CeO_2 , (b) $\text{V}_{0.025}\text{Ce}$, (c) $\text{V}_{0.05}\text{Ce}$, (d) $\text{V}_{0.1}\text{Ce}$, (e) $\text{V}_{0.2}\text{Ce}$, and (f) VO_x .

The bands presented at 2932–2933 and 2837–2843 cm^{-1} attributed to the asymmetric and symmetric stretching of methyl (CH_3) could be observed over CeO_2 and $\text{V}_{0.025}\text{Ce}$, respectively, which was attributed to the generation of CH_3CHO and CH_3COOH intermediates during the 1,2-DCE oxidation process [45]. On the other hand, no bands could be detected over the $\text{V}_{0.05}\text{Ce}$ catalyst in the above wavenumber range. The weak bands located at 3036–3032 cm^{-1} were detected over $\text{V}_{0.1}\text{Ce}$ ($>150^\circ\text{C}$) and $\text{V}_{0.2}\text{Ce}$ ($>180^\circ\text{C}$) catalysts, which corresponded with the asymmetric stretching of methylene species ($-\text{CH}_2-$) [15,45]. VO_x exhibited two weak bands at 3064 and 2931 cm^{-1} corresponding to antisymmetric stretching of methylene species and antisymmetric stretching of methyl (CH_2), respectively [45]. Generally, the vibration of $-\text{CH}-$ stretching ($\nu(\text{CH})$, such as CH_2- and CH_3- groups) is related to the adsorption of 1,2-DCE on the catalyst surface [46]. The bands present between 2400 and 2300 cm^{-1} were associated with CO_2 adsorption, while the bands located in the 2300–2000 cm^{-1} region were indexed to CO adsorption [15,43]. As shown in Figure 10b,c, no bands corresponding to adsorbed CO_2 were detected over $\text{V}_{0.025}\text{Ce}$ and

$V_{0.05}\text{Ce}$ catalysts, and the bands corresponding to adsorbed CO could not be observed in all catalysts. The bands at $1700\text{--}1200\text{ cm}^{-1}$ could be classified as the vibration of surface formates, carbonate species, and hydrocarbons, which were associated with the formation of CO_2 and CO during 1,2-DCE oxidation [24].

For all catalysts, the bands present at $1666\text{--}1610\text{ cm}^{-1}$ were considered as C=C stretching vibration [30]. The intensity of the stretching vibration of C=C over $V_{0.1}\text{Ce}$ and $V_{0.2}\text{Ce}$ catalysts gradually decreased with increasing temperature and finally disappeared at relative high temperature. The band deemed as C=O stretching vibration (ca. 1693 cm^{-1}) could be found over VO_x [43]. The characteristic bands appearing at $1587\text{--}1532\text{ cm}^{-1}$ corresponding to the carboxylate $\nu(\text{COO}^-)$ asymmetric stretching of acetate species could be detected over all catalysts [47]. The bands located at $1429\text{--}1409\text{ cm}^{-1}$ associated with the formation of $-\text{CH}_2-$ and $-\text{CH}-$ groups (e.g., $\delta(\text{CH}_2\text{Cl})$, $\delta(\text{HCCl})$, and $\delta(\text{CCH})$) could be detected over all catalysts (except $V_{0.1}\text{Ce}$), illustrating that 1,2-DCE was adsorbed and activated [15,43]. The intensity of bands over these catalysts primarily increased and then decreased with escalating temperature, inferring that 1,2-DCE oxidation occurred [15]. Bands located at $1332\text{--}1364\text{ cm}^{-1}$ over VO_x/CeO_2 catalysts could be detected, which were ascribed to the partial oxidized surface species as acetates, maleate species, and formates [47]. The bands presented at $1138\text{--}1120\text{ cm}^{-1}$ were indexed to the vibration stretching of $-\text{CH}-$. The bands at $1284\text{--}1292\text{ cm}^{-1}$ over CeO_2 and $V_{0.025}\text{Ce}$ catalysts could be attributed to $-\text{CH}-$ vibration groups [48]. The band present at 1209 cm^{-1} could be indexed to phenolate ($\nu(\text{CH})/\nu(\text{CO})$) over CeO_2 . Moreover, the bands over VO_x located at 1269 , 1234 , and 1180 cm^{-1} could be identified as the formation of $-\text{CH}_2-$ and $-\text{CH}-$ groups, suggesting that 1,2-DCE was adsorbed and activated over the catalyst.

Combining the results of in situ DRIFTS and byproduct distribution (Figures 9 and 10), a destruction mechanism of 1,2-DCE over prepared materials was proposed, as shown in Scheme 1. Generally, the catalytic oxidation of chlorinated alkanes (CA) proceeds according to the procedure of CA adsorption $\rightarrow$ Cl dissociation $\rightarrow$ C–C/C–Cl cleavage $\rightarrow$ Cl desorption/accumulation [49,50]. As such, 1,2-DCE is initially adsorbed on the surface of catalysts, which is mainly ascribed with the adsorption and dissociation of Cl bonds on Lewis acid sites ($\text{V}^{5+/4+}$ and $\text{Ce}^{4+/3+}$) [15]; The C–Cl (Path 1) and C–C (Path 2) bonds in 1,2-DCE are activated and cleaved, forming chloroethane, vinyl chloride, and chloromethane intermediates. Afterward, the polychlorinated byproducts (CHCl_3 , CCl_4 , C_2HCl_3 , and $\text{C}_2\text{H}_3\text{Cl}_3$) are mainly produced via dehydrochlorination and chlorination. Then, the reaction of dissociative Cl from polychlorinated byproducts and surface hydroxy groups can form HCl, and HCl would be partially oxidized to form Cl_2 (the Deacon reaction) [15,49]. Additionally, the intermediate acetaldehyde (from the activation of the C–H bond and the transformation of hydrogen species on VO_x species [15]) would be easily and rapidly oxidized to oxygenate species (carbonate bidentate) and partially oxidized to maleates, acetates, formates, and so on, which are usually considered the main source for the generation of CO and CO_2 [24,51]. The above oxygenate species are further oxidized to form the final products (CO , CO_2 , Cl_2 , and HCl).

Scheme 1. Proposed 1,2-DCE destruction mechanism over prepared catalysts.

4.3. Effect of Water Vapor

It is of great importance to study the influence of water vapor on the reaction activity of samples for CVOC destruction. Here, water vapor with different concentrations (1–5 vol.%) was introduced to study the influence of water vapor on the activity of the $V_{0.05}\text{Ce}$ catalyst in 1,2-DCE oxidation (Figure 11a). The conversion of 1,2-DCE was maintained at approximately 94% without water vapor. Interestingly, when 1, 2, or 5 vol.% of water vapor was injected into the atmosphere, 1,2-DCE conversion over the $V_{0.05}\text{Ce}$ catalyst increased slightly and was maintained at approximately 97%, 96%, or 95%, respectively, owing to that low concentration of water molecules efficiently removing Cl species from the catalyst surface [52]. However, the promotion effect of water vapor gradually decreased with increasing concentration because of the competitive adsorption or blockage of water molecules on active sites [17,52]. In addition, the catalytic activity of $V_{0.05}\text{Ce}$ was restored to the initial level when water vapor was removed from the reaction atmosphere, indicating that the $V_{0.05}\text{Ce}$ catalyst had good water resistance and stability under the conditions with/without water vapor during 1,2-DCE destruction. The effect of water vapor on chlorinated byproduct distribution over the $V_{0.05}\text{Ce}$ catalyst was further investigated, as exhibited in Figure 10b–d. It was found that the presence of water vapor did not change the type of chlorinated byproducts; however, the yields of CHCl_3 , CCl_4 , and C_2HCl_3 over the $V_{0.05}\text{Ce}$ catalyst were apparently lower than those in the absence of water vapor because the reactivity of Cl_2 was inhibited by water molecules as a hydrogen source [7,49]. Moreover, the yield of chlorinated byproducts decreased with increasing water vapor concentration, suggesting that the presence of water vapor could efficiently inhibit the generation of chlorinated byproducts during 1,2-DCE oxidation.

Figure 11. (a) Effects of water on 1,2-DCE conversion over $V_{0.05}\text{Ce}$ catalyst; (b) CHCl_3 , (c) CCl_4 , and (d) C_2HCl_3 distribution during the stability test.

4.4. Key Factors Inhibiting the Formation of Chlorinated Intermediate Species

Figure 9 reveals that the yields of chlorinated byproducts (CHCl_3 , CCl_4 , C_2HCl_3 , and $\text{C}_2\text{H}_3\text{Cl}_3$) over VO_x/CeO_2 were significantly lower than those of CeO_2 and VO_x during the 1,2-DCE oxidation process, ascribed to the high surface Cl removal ability of composite catalysts. Feng et al. [24] reported that the CoCrO_x catalyst can effectively inhibit the yield of chlorinated byproducts during 1,2-DCE destruction, and it possesses better product selectivity than Cr_2O_3 and Co_3O_4 due to the abundant B and L acid sites and higher acid strength. Therefore, the relationship between chlorinated byproducts yield and total acidity over VO_x/CeO_2 catalysts was analyzed. As shown in Figure 12a, CHCl_3 , CCl_4 , C_2HCl_3 , and $\text{C}_2\text{H}_3\text{Cl}_3$ yields versus total acidity maintained linear relationships ($R^2 = 0.996, 0.991, 0.993$, and 0.997 , respectively). Compared with $\text{V}_{0.025}\text{Ce}$, $\text{V}_{0.1}\text{Ce}$, and $\text{V}_{0.2}\text{Ce}$ catalysts, $\text{V}_{0.05}\text{Ce}$ possessed higher total acidity and lower chlorinated byproduct (CHCl_3 , CCl_4 , C_2HCl_3 , and $\text{C}_2\text{H}_3\text{Cl}_3$) yields, indicating that the yields of chlorinated byproducts decreased with increasing total acidity, which apparently reduced the occurrence of the chlorination reaction [53]. In addition, the catalytic activity of VO_x/CeO_2 catalysts (T_{90}) versus total acidity maintained a good linear relationship ($R^2 = 0.995$), as shown in Figure 12b. The above results indicate that the total acidity of catalysts played a vital role in inhibiting the production of chlorinated byproducts. Therefore, it can be reasonably explained that the low chlorinated byproduct yields could be ascribed to the higher total acidity and good synergy between CeO_2 and VO_x species during the 1,2-DCE oxidation process.

Figure 12. (a) Relationship between chlorinated byproduct yields and total acidity over VO_x/CeO_2 catalysts; (b) relationship between T_{90} of VO_x/CeO_2 catalysts and total acidity.

4.5. Characterization of the Used Catalysts

XRD and XPS analyses of the used $\text{V}_{0.05}\text{Ce}$ catalyst were carried out, and the results are summarized in Figure 13 and Table S1 (Supplementary Materials). Compared to the fresh $\text{V}_{0.05}\text{Ce}$ catalyst, the crystal phase of CeO_2 of the used $\text{V}_{0.05}\text{Ce}$ catalyst remained unchanged, indicating that the phase of CeO_2 was not destroyed by the attack of Cl species, further confirming that the $\text{V}_{0.05}\text{Ce}$ catalyst possessed excellent resistance to chlorine poisoning (Figure 13a). Figure 13b shows that the lattice oxygen (O_α) species abundance of the used $\text{V}_{0.05}\text{Ce}$ catalyst was lower than that of the fresh $\text{V}_{0.05}\text{Ce}$ catalyst, indicating that a large number of lattice oxygen species were removed, giving rise to the greater formation of Ce^{3+} species (Table S1, Supplementary Materials) [35]. We discovered that the Ce^{3+} species abundance of the used $\text{V}_{0.05}\text{Ce}$ catalyst was remarkably higher than that of the fresh $\text{V}_{0.05}\text{Ce}$ catalyst, confirming that the lattice oxygen species was removed leading to the greater formation of Ce^{3+} species (Figure 13c and Table S1, Supplementary Materials). Additionally, greater Ce^{3+} species abundance led to greater formation of surface oxygen vacancies, with surface oxygen species being adsorbed onto oxygen vacancies over time, showing that the $\text{V}_{0.05}\text{Ce}$ catalyst owned superior catalytic performance (Figure 13b and Table S1, Supplementary Materials). No V^{4+} species over the used $\text{V}_{0.05}\text{Ce}$ catalyst

could be detected, suggesting that the V^{4+} species were completely transformed into V^{5+} species ($V^{4+} \rightarrow V^{5+}$), accelerating the oxidation of 1,2-DCE (Figure 13d). According to the above results, it was confirmed that the Ce^{3+} species and surface oxygen (O_β) species are important factors in improving the catalytic performance of the $V_{0.05}Ce$ catalyst.

Figure 13. (a) XRD of the used $V_{0.05}Ce$ catalyst; XPS spectra of the used $V_{0.05}Ce$ catalyst: (b) O 1s, (c) Ce 3d, and (d) V 2p.

The Cl 2p spectra of all used catalysts were also further employed to investigate the chlorine deposit over catalysts, as displayed in Figure S5 (Supplementary Materials). The peaks at 198.1–198.5 eV were assigned to HCl and/or Cl_2 , while the peaks at 198.1–198.5 eV were ascribed to the adsorption of 1,2-DCE on the catalyst surface [36]. It was revealed that CeO_2 had two peaks respectively ascribed to the HCl (and/or Cl_2) species and the adsorption of 1,2-DCE on the catalyst surface. However, the adsorption peak of 1,2-DCE on the catalyst surface could not be observed over CeO_2-C . It was speculated that the 1,2-DCE did not directly contact the surface of the catalyst during the reaction process, which could explain the poor catalytic performance of the CeO_2-C catalyst. HCl (and/or Cl_2) species and the adsorption of 1,2-DCE on the catalyst surface over VO_x/CeO_2 catalysts (except $V_{0.05}Ce$) could be detected. Unexpectedly, no peaks could be discovered over $V_{0.2}Ce$ and VO_x catalysts, potentially due to the formation of chlorinated oxide rather than HCl (and/or Cl_2) species.

4.6. Key Factors for 1,2-DCE Oxidation

Combining the results of the surface properties (XRD and XPS) of the used $V_{0.05}Ce$ catalyst, it was discovered that the lattice oxygen (O_α) species abundance of the used $V_{0.05}Ce$ catalyst was lower than that of the fresh $V_{0.05}Ce$ catalyst and the Ce^{3+} species abundance of the used $V_{0.05}Ce$ catalyst was remarkably higher than that of the fresh $V_{0.05}Ce$ catalyst. Moreover, the surface oxygen species abundance adsorbed on the oxygen vacancies of the $V_{0.05}Ce$ catalyst increased after the stability test. Therefore, the large

number of Ce^{3+} species could enhance the formation of oxygen vacancies, which could effectively accelerate the mobility of active oxygen species and consequently promote the catalytic activity. According to the results of H_2 -TPR, it was revealed that both the total H_2 consumption amount and the initial H_2 consumption rate of catalysts followed the sequence of $\text{V}_{0.05}\text{Ce} > \text{V}_{0.1}\text{Ce} > \text{V}_{0.025}\text{Ce} > \text{CeO}_2 > \text{V}_{0.2}\text{Ce}$, suggesting that $\text{V}_{0.05}\text{Ce}$ had superior low-temperature reducibility, effectively promoting the low-temperature reaction of 1,2-dichloroethane. The relationship between chlorinated byproduct yields and total acidity over VO_x/CeO_2 catalysts was also analyzed. It was found that CHCl_3 , CCl_4 , C_2HCl_3 , and $\text{C}_2\text{H}_3\text{Cl}_3$ yields versus total acidity maintained linear relationships ($R^2 = 0.996, 0.991, 0.993$, and 0.997 , respectively). Compared with $\text{V}_{0.025}\text{Ce}$, $\text{V}_{0.1}\text{Ce}$, and $\text{V}_{0.2}\text{Ce}$ catalysts, $\text{V}_{0.05}\text{Ce}$ possessed higher total acidity and lower chlorinated byproduct (CHCl_3 , CCl_4 , C_2HCl_3 , and $\text{C}_2\text{H}_3\text{Cl}_3$) yields, indicating that the yields of chlorinated byproducts decreased with increasing total acidity. Moreover, the catalytic activity of VO_x/CeO_2 catalysts (T_{90}) versus total acidity maintained a good linear relationship ($R^2 = 0.995$). The above results indicated that the low chlorinated byproduct yields could be ascribed to higher total acidity during 1,2-DCE oxidation process. The influence of water vapor on the formation of chlorinated byproducts was also studied. It was displayed that the presence of water vapor did not change the type of chlorinated byproducts; however, the yields of CHCl_3 , CCl_4 , and C_2HCl_3 over the $\text{V}_{0.05}\text{Ce}$ catalyst were apparently lower than those in the absence of water vapor because the reactivity of Cl_2 was inhibited by water molecules as a hydrogen source. Moreover, the yield of chlorinated byproducts decreased with increasing water vapor concentration, suggesting that the presence of water vapor could efficiently inhibit the generation of chlorinated byproducts during 1,2-DCE oxidation.

5. Conclusions

In this work, hollow nanosphere-like VO_x/CeO_2 materials were prepared using a wetness impregnation route and tested for 1,2-DCE destruction. The superior low-temperature reducibility and the mobility of O^- and O_2^- species (chemically adsorbed oxygen species) ensured the superior catalytic activity, catalytic stability, and superior resistance to chlorine poisoning of the $\text{V}_{0.05}\text{Ce}$ catalyst for 1,2-DCE oxidation. The generation of chlorinated byproducts (e.g., CHCl_3 , CCl_4 , C_2HCl_3 , and $\text{C}_2\text{H}_3\text{Cl}_3$) derived from the cleavage of C–C and C–Cl bonds of 1,2-DCE was inhibited owing to the abundant acid sites and synergy between VO_x and CeO_2 . Water vapor (1–5 vol.%) had a promoting effect on the activity of $\text{V}_{0.05}\text{Ce}$, which was ascribed to the efficient removal of Cl species on the surface.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2227-9717/9/1/119/s1>: Figure S1. XRD profiles of $\text{CeO}_2\text{-C}$ catalyst; Figure S2. HAADF-STEM images of $\text{CeO}_2\text{-C}$ catalyst; Figure S3. Nitrogen adsorption/desorption isotherms of $\text{CeO}_2\text{-C}$ catalyst; Figure S4. Pore size distribution of $\text{CeO}_2\text{-C}$ catalyst; Figure S5. Cl 2p XPS spectra of the used catalysts; Figure S6. CO_x selectivity of prepared catalysts; Table S1. XPS results of used $\text{V}_{0.05}\text{Ce}$ catalyst.

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