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Elimination of 1,2-dichloroethane over $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts: synergistic performance between oxidizing ability and acidity

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ABSTRACT

A series of $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts with different $(\text{Ce,Cr})_x\text{O}_2$ to Nb_2O_5 mass ratios were synthesized by the deposition-precipitation method for use in deep catalytic oxidation of 1,2-dichloroethane (DCE), which is one of the typical chlorinated volatile organic compound pollutants. The textural properties were characterized by X-ray diffraction, N_2 adsorption/desorption isotherms, UV-Raman spectroscopy, and scanning electron microscopy. The surface acidity and the redox properties were characterized by ammonia temperature-programmed desorption and H_2 temperature-programmed reduction, respectively. The results show that the addition of a proper amount of $(\text{Ce,Cr})_x\text{O}_2$ over Nb_2O_5 significantly improves the intrinsic catalytic activity towards the deep oxidation of DCE, and only a very small amount of $\text{C}_2\text{H}_3\text{Cl}$ is detected as the byproduct of the oxidation process. Further study reveals the existence of an obvious synergistic effect between Nb_2O_5 , with abundant strong acid sites, and $(\text{Ce,Cr})_x\text{O}_2$, with strong oxidation sites, as the strong acid sites of Nb_2O_5 promote the adsorption and dehydrochlorination of DCE, while the strong oxidation sites of $(\text{Ce,Cr})_x\text{O}_2$ contribute to the deep oxidation of the reactant, intermediates, and byproducts.

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1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs) such as 1,2-dichloroethane (DCE) are widely used and released to the atmosphere through several industrial operations [1,2]. These compounds are well known for their high volatility, toxicity, and stability, and can be greatly harmful to both human health and the environment [1–4]. Therefore, the elimination of gas pollutants containing low concentration CVOCs is of significance. Compared to other techniques (such as adsorption, absorption condensation, and burning), deep catalytic oxidation [5–7] has been deemed as one of the most effective methods because of its high efficiency, low energy consumption, and the

absence of secondary pollution.

Up to now, two types of catalysts have been commercially applied to the deep catalytic oxidation process: supported noble metal [2,3,6] and metal oxide catalysts [2,3,8]. Although supported noble metal catalysts generally exhibit higher oxidation activities, they react more easily with chlorine species, leading to the poisoning of the catalysts and the formation of polychlorinated byproducts during the oxidation process. Therefore, metal oxide catalysts, especially CeO_2 -based mixed oxides (such as $\text{CeO}_2\text{-MnO}_x$, $\text{CeO}_2\text{-ZrO}_2$, and $\text{Ce}_x\text{Pr}_{1-x}\text{O}_2$) [9–12] have been investigated and used extensively, owing to their lower cost and better resistance to chlorine poisoning. Among them, $(\text{Ce,Cr})_x\text{O}_2$ exhibits outstanding catalytic performance for

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the deep oxidation of Cl-VOCs owing to its high oxidizing ability, but it is still necessary to increase its selectivity to HCl rather than towards Cl_2 , in order to reduce the toxicity of the final products [11,13–15]. On the other hand, various researchers [16–19] have reported that H-type zeolites exhibit high selectivities to HCl formation for the degradation of Cl-VOCs owing to their proper strong/weak acid properties. However, notable formations of CO and byproducts, as well as obvious deactivation by coking, are observed at the same time, caused by the lack of sufficient oxidation sites [20,21]. Thus, both the acid and oxidation properties need to be improved to further realize a desirable catalytic performance. High-valence metal oxides (TiO_2 , WO_3 , MoO_3 , and Nb_2O_5) [22–27] with abundant acid sites are well known as “solid-acid” catalysts and are widely used in acid-catalyzed and redox reactions. Therefore, a combination of $(\text{Ce,Cr})_x\text{O}_2$ mixed oxides with solid-acid metal oxides would be beneficial, rendering such materials promising for the catalytic oxidation of Cl-VOCs.

Based on the previous investigations mentioned above, in this study, Nb_2O_5 was chosen as a prospective solid-acid support material, and a series of $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts with different $(\text{Ce,Cr})_x\text{O}_2$ to Nb_2O_5 mass ratios were synthesized by a deposition-precipitation method and their performance for the deep catalytic oxidation of DCE was evaluated. The catalysts were further characterized by means of X-ray diffraction (XRD), N_2 adsorption-desorption, UV-Raman, scanning electron microscopy (SEM), ammonia temperature-programmed desorption (NH_3 -TPD), and H_2 temperature-programmed reduction (H_2 -TPR) techniques. The objective of this study was to obtain a satisfactory activity and selectivity for DCE oxidation by regulating the active components, while obtaining some insight into the synergy between the acid sites and the oxidation sites of the $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalyst system.

2. Experimental

2.1. Catalyst preparation

The support material Nb_2O_5 was purchased from Guoyao Company and calcined in air (500 °C, 2 h), followed by mechanical milling for 0.5 h. $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ mixed oxides with different $(\text{Ce,Cr})_x\text{O}_2$ to Nb_2O_5 mass ratios were synthesized by the traditional deposition-precipitation method. First, a certain amount of Nb_2O_5 was added into a solution mixed with quantified amounts of $\text{Ce}(\text{NO}_3)_3$ and $\text{Cr}(\text{NO}_3)_3$ (molar ratio of Ce/Cr was 4:1), and then, ultrasonic concussion was performed for 1 h. Afterwards, 0.50 mol L^{-1} $(\text{NH}_4)_2\text{CO}_3$ was added dropwise to the above mixed solution under vigorous stirring under vigorous stirring until the final pH of the solution reached 9.0. Upon aging at 25 °C for 12 h, the precipitated solids were filtered, washed with distilled water, and then dried in ethanol under supercritical conditions (265 °C, 2 h, 7.5 MPa). The solids were subsequently calcined in air at 500 °C for 2 h. The obtained samples were named as $y(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$, with the mass ratio y of $(\text{Ce,Cr})_x\text{O}_2$ to Nb_2O_5 being 4, 2, 1, 0.75, 0.5, 0.25, 0.1, and 0.05. For comparison, a $(\text{Ce,Cr})_x\text{O}_2$ mixed oxide was also prepared by following a similar procedure. All the samples were

finally pressed into pellets and sieved to 40–60 mesh (0.3–0.45 mm) before use.

2.2. Catalyst characterizations

The XRD patterns of the samples were recorded on a D/Max-2550pc powder diffractometer by using $\text{Cu K}\alpha$ radiation. The X-ray tube was operated at 40 kV and 250 mA, and the powder diffractogram was recorded at 0.02° intervals in the 2θ range 10°–90°, with the scanning rate being 5°/min.

The N_2 adsorption/desorption isotherms of the samples were obtained at –196 °C by using a Micromeritics TristarII automatic adsorption instrument. The samples were pretreated under high vacuum at 200 °C for 4 h before the measurements.

The UV-Raman spectra of the samples were obtained on a LabRam-HR800 instrument using 325 nm He-Gd as the laser source; the spectral resolution was 4 cm^{-1} . The scanning range was 150–2000 cm^{-1} .

The SEM images were recorded on a SU1510 apparatus.

NH_3 -TPD was performed in a quartz fixed-bed microreactor equipped with a TCD detector. Prior to the adsorption of ammonia, the catalyst (about 100 mg) was pretreated in a N_2 stream (99.99%, 35 mL min^{-1}) at 500 °C for 0.5 h. After cooling to 100 °C, the catalyst was exposed to a flow (30 mL min^{-1}) of 20 vol% NH_3/N_2 mixture for 0.5 h, and then treated in pure N_2 flow for 1 h in order to remove the physically adsorbed NH_3 . Finally, desorption experiment was carried out in pure N_2 flow (40 mL min^{-1}) from 100 to 600 °C at the heating rate of 10 °C min^{-1} . All these profiles were simulated by Gaussian functions.

The redox properties of the catalysts were examined by H_2 -TPR experiments. The catalyst (100 mg, 40–60 mesh) was placed in a U quartz reaction tube and pretreated in N_2 flow (99.999%, 30 mL min^{-1}) at 200 °C for 30 min, before being cooled to 100 °C. The reduction process was performed in 5 vol% H_2/Ar (40 mL min^{-1}) between 50 and 900 °C, with the heating rate being 10 °C min^{-1} . The H_2 consumption was detected on-line by a gas chromatograph (GC 1690, China) that was equipped with a TCD.

2.3. Catalytic activity tests

The catalytic performance tests of the catalysts were conducted in a microreactor (quartz tube, 6 mm i.d.) at atmospheric pressure, with the gas hourly space velocity being 15000 h^{-1} . The feed flowing through the microreactor consisted of 1000 ppmv DCE, with dry air as the balance gas, and the total flow was 75 mL min^{-1} . A mass of 500 mg of the catalyst (40–60 mesh) was loaded. The concentrations of DCE, any possible organic byproducts, and CO_x in the effluent gas were analyzed on-line by using the gas chromatograph that was equipped with an FID and a TCD. The concentrations of HCl and Cl_2 in the effluent gas were measured by bubbling the waste gases through 0.0125 mol L^{-1} NaOH solution for 20 min when DCE was completely converted. The Cl^- concentration was measured by a Cl^- selective electrode, whereas the Cl_2 concentration was determined through chemical titration with ferrous am-

monium sulfate by using *N,N*-diethyl-*p*-phenylenediamine sulfate as the indicator. The HCl selectivity was calculated as $S_{\text{HCl}} = [\text{HCl}] / ([\text{HCl}] + [\text{Cl}_2])$.

3. Results and discussion

3.1. Evaluation of the catalytic performance

The performance of the obtained catalysts for the degradation of DCE is presented in Fig. 1(A). Previous tests have revealed that the mass transfer limitation is absent under this test condition, and no obvious DCE conversion is observed below 420 °C in the blank experiment. As shown in Fig. 1(A), the $T_{50\%}$ (the temperature needed to achieve 50% conversion) of Nb_2O_5 is about 304 °C, and DCE can be completely converted at 360 °C. Obvious improvements in the catalytic activities can be observed by introducing $(\text{Ce,Cr})_x\text{O}_2$, as all the $y(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts are able to fully convert DCE below 300 °C. The $T_{50\%}$ values of $y(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts tend to decrease first and then increase with increasing $(\text{Ce,Cr})_x\text{O}_2$ to Nb_2O_5 mass ratio, although all the mixed oxide catalysts show slightly higher $T_{50\%}$ compared to single $(\text{Ce,Cr})_x\text{O}_2$. To better verify the intrinsic catalytic activity, the TOF values were obtained at 150 °C, and the results are shown in Fig. 1(B). All the mixed catalysts show larger TOF values than the single $(\text{Ce,Cr})_x\text{O}_2$ catalyst. Moreover, 0.25 $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalyst exhibits a noticeable intrinsic catalytic activity owing to its largest TOF value, and its $T_{90\%}$ is almost similar to that of $(\text{Ce,Cr})_x\text{O}_2$. These results indicate that there exists a synergistic effect between $(\text{Ce,Cr})_x\text{O}_2$ and Nb_2O_5 . Such an effect can contribute to improving the intrinsic activities of the mixed oxide catalysts.

For the catalytic elimination of Cl-VOCs, any possible by-products should be detected carefully, since they may be more toxic and more difficult to destroy. As shown in Fig. 1(C), within the detection limits of the TCD and FID used, $\text{C}_2\text{H}_3\text{Cl}$ is the sole byproduct observed during the DCE oxidation, and no other possible byproducts (such as phosgene, chloroform, CCl_4 , and dioxins) are detected over these investigated catalysts. A noticeable amount of $\text{C}_2\text{H}_3\text{Cl}$ is detected over Nb_2O_5 , as the concentration (38 ppm) of $\text{C}_2\text{H}_3\text{Cl}$ is maximum at 400 °C; $\text{C}_2\text{H}_3\text{Cl}$ is not eliminated even at 480 °C. For the $y(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts, both the maximum $\text{C}_2\text{H}_3\text{Cl}$ concentration and the peak temperature decrease obviously with increasing $(\text{Ce,Cr})_x\text{O}_2$ to

Table 1

Results of S_{HCl} , XRD, and N_2 adsorption/desorption measurements.

Catalyst	S_{HCl}^a (%)	Crystallite size of CeO_2 (nm)	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
$(\text{Ce,Cr})_x\text{O}_2$	74.9	6.5	99.0	0.268	11.2
4 $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$	81.6	6.3	77.4	0.265	16.1
2 $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$	87.4	6.3	70.9	0.264	16.1
$(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$	90.5	6.2	60.9	0.196	13.0
0.75 $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$	90.8	6.1	60.7	0.169	11.8
0.5 $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$	92.1	5.7	51.9	0.138	11.5
0.25 $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$	96.2	4.5	46.0	0.119	10.8
0.1 $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$	98.7	—	45.8	0.113	10.2
0.05 $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$	99.4	—	45.7	0.106	10.1
Nb_2O_5	99.7	—	44.3	0.100	8.8

^a Measured at 320 °C, whereas for Nb_2O_5 the reaction temperature was 480 °C.

Nb_2O_5 mass ratio. This result indicates that the synergistic effect between $(\text{Ce,Cr})_x\text{O}_2$ and Nb_2O_5 not only is beneficial for degrading DCE into $\text{C}_2\text{H}_3\text{Cl}$, but also facilitates $\text{C}_2\text{H}_3\text{Cl}$ oxidation.

For the complete oxidation of DCE, the final products are CO/CO_2 , HCl/Cl_2 , and H_2O . The S_{HCl} (selectivity to HCl) data of all these catalysts is presented in Table 1. All the $y(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts reveal high selectivities toward the desired HCl and CO_2 (more than 98%, not listed). Nb_2O_5 alone shows the highest selectivity to HCl. As the $(\text{Ce,Cr})_x\text{O}_2$ to Nb_2O_5 mass ratio increases, S_{HCl} gradually decreases. This can be explained in terms of the partial oxidation of HCl into Cl_2 [21,28], due to the strong oxidation ability of $(\text{Ce,Cr})_x\text{O}_2$.

3.2. Catalyst characterization

3.2.1. Structural/textural properties

Fig. 2 displays the XRD patterns of all the catalysts, and Table 1 lists the corresponding crystallite sizes. The characteristic diffraction peaks of TT-phase Nb_2O_5 (at $2\theta = 22.6^\circ, 28.5^\circ, 36.7^\circ, 46.2^\circ$, and 50.6°) [29] and cubic CeO_2 (at $2\theta = 28.6^\circ, 33.0^\circ, 47.6^\circ$, and 56.4°) [21] appear for $y(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts. On the other hand, the characteristic diffraction peaks of Cr_2O_3 (at $2\theta = 33.6^\circ, 36.3^\circ$, and 54.9°) [28] are not detected, which can be attributed either to the low content of the Cr species or the high dispersion of the Cr species in the CeO_2 matrix. As the $(\text{Ce,Cr})_x\text{O}_2$ to Nb_2O_5 mass ratio increases, the diffraction peaks of CeO_2 become sharper and the peak intensities increase, re-

Fig. 1. Catalytic performance for DCE elimination over $y(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$. (A) DCE conversion; (B) TOF values (obtained at 150 °C) and $T_{50\%}$; (C) Concentration of $\text{C}_2\text{H}_3\text{Cl}$ byproduct.

Fig. 2. XRD patterns of $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts.

vealing the formation of large CeO_2 crystallites. The CeO_2 crystallite size in the $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts varies between 4.5 and 6.3 nm, which is smaller than that of single $(\text{Ce,Cr})_x\text{O}_2$ (6.5 nm) (a TEM image and the particle size counts of $(\text{Ce,Cr})_x\text{O}_2$ are shown in Fig. S1, Supporting Information); this is because the large surface area of Nb_2O_5 favors the dispersion of $(\text{Ce,Cr})_x\text{O}_2$. Together with the results of the catalytic performance evaluation, we can see that $(\text{Ce,Cr})_x\text{O}_2$ is highly dispersed on the Nb_2O_5 surface when the $(\text{Ce,Cr})_x\text{O}_2$ to Nb_2O_5 mass ratio is less than 0.25, thus, the synergistic effect between $(\text{Ce,Cr})_x\text{O}_2$ and Nb_2O_5 is enhanced, and the catalytic activity is further promoted. When the $(\text{Ce,Cr})_x\text{O}_2$ to Nb_2O_5 mass ratio exceeds 0.25, the catalytic activity slightly decreases, possibly due to a worse surface dispersion of $(\text{Ce,Cr})_x\text{O}_2$ or the less exposed surface acid centers of Nb_2O_5 .

Raman spectroscopy is considered to be a useful tool for obtaining additional structural information related to lattice vibrations that is sensitive to crystal symmetry. The UV-Raman profiles of all the $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts are presented in Fig. 3. All the catalysts show a characteristic peak at 325 cm^{-1} , which is attributed to the LO vibration mode that is related to

Fig. 3. UV-Raman patterns of $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts.

the defect spaces of the O vacancies present in the metal oxide lattice. For Nb_2O_5 support, two peaks at 687 and 810 cm^{-1} can be observed, which can be assigned to the symmetrical stretching vibrations of the Nb–O bonds in both the surface $\text{Nb}_2\text{O}_5[\text{NbO}_6]$ and the $[\text{NbO}_4]$ structure [30,31]. For $(\text{Ce,Cr})_x\text{O}_2$ catalysts, three peaks appear at 460, 587, and 1176 cm^{-1} , which can be assigned to the symmetrical stretching vibrations of the Ce–O bonds in the $[\text{CeO}_4]$ structure [14,30,31]. For the $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts, increasing the $(\text{Ce,Cr})_x\text{O}_2$ content leads to decreases in the intensities of the peaks observed at 325 and 687 cm^{-1} . When the $(\text{Ce,Cr})_x\text{O}_2$ to Nb_2O_5 mass ratio exceeds 0.25, the characteristic peak of CeO_2 can be clearly observed, and the peak intensity increases with increasing mass ratio. No Raman signal corresponding to Cr_2O_3 is observed, which agrees well with the XRD result. Moreover, the peak at 687 cm^{-1} shifts to a lower wavenumber over mixed oxide catalysts, compared to that observed over Nb_2O_5 , which indicates the existence of a strong interaction between $(\text{Ce,Cr})_x\text{O}_2$ and Nb_2O_5 [30,31].

The results of the N_2 adsorption-desorption characterizations are displayed in Fig. 4 and Table 1. It can be seen that the $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts are mesoporous materials, as the pore diameters are mainly distributed around 4 and 8 nm. Increasing the $(\text{Ce,Cr})_x\text{O}_2$ content results in larger specific surface areas and pore volumes (see Table 1), as well as broader pore size distributions. In combination with the results of the catalytic performance tests, it can be seen that the activities of the $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ mixed oxide catalysts are not directly linked to their pore diameters or pore size distributions. Moreover, the BET specific surface areas and the pore volumes of the materials are not consistent with the trend of their catalytic activities. Such results indicate that these textural properties may not be the main factors responsible for the improved catalytic activity of this system.

3.2.2. Morphological characterization

The SEM images of the samples are displayed in Fig. 5. As shown in Fig. 5(A)–(F), mono-component $(\text{Ce,Cr})_x\text{O}_2$ and Nb_2O_5 presents distinctively different morphologies, as Nb_2O_5 exhibits

Fig. 4. Pore size distributions of $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts.

Fig. 5. SEM images of (A) Nb₂O₅, (B) 0.1(Ce,Cr)_xO₂/Nb₂O₅, (C) 0.25(Ce,Cr)_xO₂/Nb₂O₅, (D) (Ce,Cr)_xO₂/Nb₂O₅, (E) 4(Ce,Cr)_xO₂/Nb₂O₅, and (F) (Ce,Cr)_xO₂ catalysts.

typical sheet structure with various particle sizes, while (Ce,Cr)_xO₂ exhibits irregular spherical morphology with relatively smaller particle sizes of approximately 4 to 7 nm (see Fig. S1.). For γ (Ce,Cr)_xO₂/Nb₂O₅ catalysts, (Ce,Cr)_xO₂ is well dispersed on the matrix of the Nb₂O₅ support. As (Ce,Cr)_xO₂ content increases, more agglomerated (Ce,Cr)_xO₂ particles are observed. For the 4(Ce,Cr)_xO₂/Nb₂O₅ catalyst, instead of fully covering the Nb₂O₅ surface, most of the (Ce,Cr)_xO₂ particles still remain dispersed in the mixed oxide system. As shown in Fig. 5(A)–(F), Nb₂O₅ exhibits the typical sheet structure with vari-

ous particle sizes, whereas (Ce,Cr)_xO₂ exhibits a rice-particle-like structure with relatively smaller particle sizes. For the γ (Ce,Cr)_xO₂/Nb₂O₅ catalysts, (Ce,Cr)_xO₂ is “snow-like” dispersed on the matrix of the Nb₂O₅ support. As the (Ce,Cr)_xO₂ content increases, more agglomerated (Ce,Cr)_xO₂ particles are observed. For 4(Ce,Cr)_xO₂/Nb₂O₅ catalyst, instead of fully covering the Nb₂O₅ surface, most of the (Ce,Cr)_xO₂ particles remain dispersed in the mixed oxide system. Therefore, for γ (Ce,Cr)_xO₂/Nb₂O₅ catalysts, appropriate contact of (Ce,Cr)_xO₂ and Nb₂O₅ is beneficial for enhancing their interaction. Meanwhile, proper exposure of the Nb₂O₅ particle surface can facilitate the synergistic effect between (Ce,Cr)_xO₂ and Nb₂O₅, which can result in better catalytic performance.

3.2.3. Acidity properties

The surface acid properties of the catalysts were characterized by NH₃-TPD measurements. The obtained profiles are shown in Fig. 6. As can be seen in Fig. 6(A), three distinct desorption peaks can be observed for all the γ (Ce,Cr)_xO₂/Nb₂O₅ catalysts. The peaks below 150 °C are considered to correspond to the desorption of the physically adsorbed NH₃. Two peaks are observed in the range 150–450 °C. The peak α appears at a lower temperature and is ascribed to the weak acid sites, whereas the peak β is observed at a higher temperature, and is assigned to the strong acid sites [28]. Compared to (Ce,Cr)_xO₂, the peak β obtained over Nb₂O₅ support shifts to a higher temperature, along with an increase in its area, indicating that Nb₂O₅ contains more strong acid sites and exhibits stronger acidity than (Ce,Cr)_xO₂. For the γ (Ce,Cr)_xO₂/Nb₂O₅ catalysts, we can see from Fig. 6(B) that the concentration of the weak acid sites increases at a higher (Ce,Cr)_xO₂ to Nb₂O₅ ratio, while the concentration of the strong acid sites and the total acidity decrease, along with the $R_{s/w}$ values (which represent the ratio of strong acid concentration to weak acid concentration). Similar results have been reported elsewhere [4,21], as the surface strong acid sites are more likely to be covered by the metal hydroxide deposited during the catalyst preparation.

The correlations between the surface acidity and the TOF values, as well as the maximum C₂H₃Cl concentrations, are shown in Fig. 6(C). It can be seen that the maximum C₂H₃Cl concentrations exhibit a positive correlation with increasing

Fig. 6. Results of NH₃-TPD measurements for γ (Ce,Cr)_xO₂/Nb₂O₅ catalysts. (A) NH₃-TPD profiles; (B) Correlations between (Ce,Cr)_xO₂ content and surface acidity; (C) Correlations between surface acidity, TOF values, and maximum C₂H₃Cl concentrations.

surface acidity. Since $\text{C}_2\text{H}_3\text{Cl}$ is recognized as the byproduct obtained during the dehydrochlorination of DCE, such a correlation reveals that the surface acid sites can promote the adsorption and dehydrochlorination of DCE to $\text{C}_2\text{H}_3\text{Cl}$. Meanwhile, the revealed order of intrinsic acidity is not consistent with the order observed for the intrinsic catalytic activity, as the TOF values tends to increase first and then decrease with increasing acidity. This result indicates that the surface acid property is not the sole factor determining the performances of the $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts.

Our previous study on the $(\text{Ce,Cr})_x\text{O}_2/\text{zeolite}$ system [21] demonstrated that both the acidic and the redox properties play important roles in the deep oxidation of CVOs. The acid sites of zeolites (especially the strong acid sites) can promote the adsorption and dehydrochlorination of DCE to $\text{C}_2\text{H}_3\text{Cl}$, whereas the high oxidizing ability of $(\text{Ce,Cr})_x\text{O}_2$ facilitates the quick oxidation of the organic byproducts to form CO_2 . The synergistic effect between the surface acid sites and the oxidation sites contributes to improving the catalytic performance. Although either the strength or the concentration of the strong acid sites over Nb_2O_5 is lower than that over HZSM-5 zeolites, it is still reasonable to assume that a similar synergistic effect exists between $(\text{Ce,Cr})_x\text{O}_2$ and Nb_2O_5 in the $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts, as the acid sites of Nb_2O_5 can promote the adsorption and dehydrochlorination of DCE to $\text{C}_2\text{H}_3\text{Cl}$, while the high oxidizing ability of $(\text{Ce,Cr})_x\text{O}_2$ can facilitate further $\text{C}_2\text{H}_3\text{Cl}$ oxidation. Such synergy can explain why the $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts show enhanced intrinsic activities during their performance evaluation.

3.2.4. Redox properties

H_2 -TPR experiments were also performed to test the reducibilities of the catalysts. Fig. 7 shows the H_2 -TPR profiles of all the $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts. For $(\text{Ce,Cr})_x\text{O}_2$, three H_2 consumption peaks are observed: peak α (at $\sim 344^\circ\text{C}$), which can be related to the reduction of Cr^{6+} to Cr^{3+} ; peak γ , which is attributed to the reduction of either surface/subsurface O or small Cr_2O_3 particles; whereas, the peak observed at a high temperature (above 700°C) can be assigned to the reduction of CeO_2 lattice O [28]. The redox properties of $(\text{Ce,Cr})_x\text{O}_2$ have

been detailedly discussed in our previous studied [11,13,28]. It is revealed that the formation of small Cr_2O_3 particles can increase the amount of oxygen vacancies in CeO_2 , which would contribute to the mobility of active oxygen species and is beneficial for the destruction of the byproducts produced in the process of DCE oxidation. The Nb_2O_5 support also shows two H_2 consumption peaks: peak β (at $\sim 410^\circ\text{C}$), attributed to the reduction of surface/subsurface O, and peak δ (at $\sim 580^\circ\text{C}$), related to the reduction of small Nb_2O_5 particles [29, 32–34]. The reduction peaks of Nb_2O_5 appear at higher temperatures and display smaller areas compared to those of $(\text{Ce,Cr})_x\text{O}_2$, indicating that its reducibility is obviously lower than that of $(\text{Ce,Cr})_x\text{O}_2$. For the $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts, as the $(\text{Ce,Cr})_x\text{O}_2$ content increases, the peak δ that corresponds to Nb_2O_5 reduction shifts to a lower temperature and eventually overlaps with the peak γ of $(\text{Ce,Cr})_x\text{O}_2$. This type of peak shift and overlap implies the possible existence of a “ $\text{Nb}^{m+}\text{-O-Ce}^{n+}$ ” strong interaction at the $(\text{Ce,Cr})_x\text{O}_2\text{-Nb}_2\text{O}_5$ interface [35,36] that can promote the reduction of Nb_2O_5 . The total peak area of “ $\gamma+\delta$ ” increases first and then decreases with increasing $(\text{Ce,Cr})_x\text{O}_2$ to Nb_2O_5 mass ratio. 0.25 $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ shows the largest “ $\gamma+\delta$ ” peak area, which suggests the strongest “ $\text{Nb}^{m+}\text{-O-Ce}^{n+}$ ” interaction among all the samples, due to the highly dispersed state of $(\text{Ce,Cr})_x\text{O}_2$ over Nb_2O_5 (as seen in the XRD and UV-Raman results). Similar trends can be seen by relating “ $\gamma+\delta$ ” peak area sequence to the catalytic activities sequence, suggesting that the redox property promoted by strong “ $\text{Nb}^{m+}\text{-O-Ce}^{n+}$ ” interaction is favorable for DCE destruction. Similarities can be observed between the trend in the “ $\gamma+\delta$ ” peak areas and that of the catalytic activities, suggesting that the redox property is favorable for DCE degradation. Besides, more Cr^{6+} species would appear with increasing $(\text{Ce,Cr})_x\text{O}_2$ content, as peak α also grows bigger with increasing $(\text{Ce,Cr})_x\text{O}_2$ content. Our previous studies [11,13,14] have demonstrated that the highly oxidizing Cr^{6+} species is beneficial for the deep oxidation of the $\text{C}_2\text{H}_3\text{Cl}$ byproduct, and thus, the maximum $\text{C}_2\text{H}_3\text{Cl}$ concentration decreases obviously with increasing $(\text{Ce,Cr})_x\text{O}_2$ to Nb_2O_5 mass ratio. However, more Cr^{6+} species does not necessarily mean better activities (see TOF values), which is another clear evidence of the fact that both the redox and the acidic properties contribute to the elimination of DCE and that a synergistic effect between $(\text{Ce,Cr})_x\text{O}_2$ and Nb_2O_5 is essential for improving the catalytic performance.

In summary, from the results detailed above, it can be seen that the synergistic effect between the redox and the acid properties plays an important role in promoting the intrinsic performance of the $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts for the deep oxidation of DCE. This synergistic effect is a result of the strong acid sites of the Nb_2O_5 support first promoting DCE adsorption and dehydrochlorination, while the strong oxidation sites of $(\text{Ce,Cr})_x\text{O}_2$ favor the deep oxidation of the reactant, intermediates, and byproducts. Proper selection of the $(\text{Ce,Cr})_x\text{O}_2$ to Nb_2O_5 mass ratio can not only enhance the existing strong metal-support interaction in $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$, but also facilitate the synergistic effect. In this study, the 0.25 $(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalyst displays the best activity. Besides, compared to our previous study on the $(\text{Ce,Cr})_x\text{O}_2/\text{HZSM-5}$ system, Nb_2O_5 exhib-

Fig. 7. H_2 -TPR curves of $\gamma(\text{Ce,Cr})_x\text{O}_2/\text{Nb}_2\text{O}_5$ catalysts.

its weaker acid and stronger redox properties than HZSM-5, therefore, less of the byproduct C_2H_3Cl is observed for $(Ce,Cr)_xO_2/Nb_2O_5$ during DCE elimination.

4. Conclusions

A series of $(Ce,Cr)_xO_2/Nb_2O_5$ catalysts with different $(Ce,Cr)_xO_2$ to Nb_2O_5 mass ratios were synthesized by the deposition-precipitation method and evaluated for the deep oxidation of DCE. Analysis of the structure and the texture of the catalysts reveal that the $(Ce,Cr)_xO_2$ mixed oxide is highly dispersed in the matrix of Nb_2O_5 support. The results of evaluation of the activities show that an appropriate $(Ce,Cr)_xO_2$ to Nb_2O_5 mass ratio (which, in this study, is 0.25) can noticeably improve the intrinsic catalytic activity for DCE elimination. Further characterizations suggest that the main reason for the catalytic performance obtained is the synergistic effect that exists between $(Ce,Cr)_xO_2$ and Nb_2O_5 . The strong acid sites of Nb_2O_5 promote the adsorption of DCE and its subsequent dehydrochlorination to form C_2H_3Cl , while the strong oxidizing ability of $(Ce,Cr)_xO_2$ contributes to the deep oxidation of the reactant, intermediates, and byproducts. Therefore, the synergy is a result of the coexistence of abundant strong acid sites and oxidation sites on the $(Ce,Cr)_xO_2/Nb_2O_5$ catalysts. The higher catalytic activity and selectivity indicate that the $(Ce,Cr)_xO_2/Nb_2O_5$ catalysts deserve more research attention and may be promising for industrial application.

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Graphical Abstract

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Elimination of 1,2-dichloroethane over $(Ce,Cr)_xO_2/Nb_2O_5$ catalysts: Synergistic performance between oxidizing ability and acidity

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A synergistic effect between $(Ce,Cr)_xO_2$ and Nb_2O_5 improves the intrinsic catalytic activity for 1,2-dichloroethane (DCE) elimination, as the acid sites of Nb_2O_5 promote DCE adsorption and dehydrochlorination, while the oxidation sites of $(Ce,Cr)_xO_2$ facilitate the deep oxidation of the intermediate C_2H_3Cl .

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(Ce,Cr)_xO₂/Nb₂O₅催化氧化1,2-二氯乙烷过程中氧化性中心与酸性中心的协同作用

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摘要: 含氯易挥发有机物(CI-VOCs)是一类常见的大气污染物, 可对生态环境和人类健康产生严重危害。相比其他治理方法, 催化氧化法具有经济、高效的优势, 其关键在于开发新型廉价的高性能催化材料。(Ce,Cr)_xO₂复合氧化物因具有强氧化性而表现出优异的催化性能, 但仍需提高HCl选择性。研究表明, 同时提高催化剂酸性和氧化性有助于促进CI-VOCs降解。Nb₂O₅等固体酸金属氧化物同时具有丰富的表面酸性中心和一定的氧化性, 被广泛应用于酸催化和氧化还原反应。将酸性氧化物和(Ce,Cr)_xO₂进行有效复合, 有望同时改善催化剂的酸性质和氧化性, 实现对CI-VOCs的高效消除。

本文选择Nb₂O₅作为固体酸载体, 采用沉积-沉淀法制备了一系列不同质量比例的复合改性y(Ce,Cr)_xO₂/Nb₂O₅催化剂, 考察了其对1,2-二氯乙烷(DCE)的催化降解性能, 并利用XRD、UV-Raman、N₂吸脱附、SEM、NH₃-TPD和H₂-TPR等手段表征了催化剂的结构-织构性质、形貌、表面酸性质以及氧化还原性能。通过优化活性组分组成, 调控复合氧化物催化剂的物理化学性质, 进一步提高其催化活性和选择性, 并深入探讨了复合氧化物之间的相互作用机制以及氧化性中心与酸性中心二者的协同催化效应对CI-VOCs催化降解性能的影响。

DCE催化降解实验结果显示, 随着(Ce,Cr)_xO₂/Nb₂O₅质量比(y值)的增加, y(Ce,Cr)_xO₂/Nb₂O₅催化剂对DCE的降解活性先增大后减小, 生成副产物C₂H₃Cl的最大浓度逐渐降低, 其中0.25(Ce,Cr)_xO₂/Nb₂O₅催化剂的本征催化活性最高。

XRD图谱显示, y(Ce,Cr)_xO₂/Nb₂O₅复合催化剂上出现了TT相Nb₂O₅和立方相CeO₂的特征峰; 当(Ce,Cr)_xO₂与Nb₂O₅质量比小于0.25时, (Ce,Cr)_xO₂在Nb₂O₅表面高度分散。UV-Raman结果显示, 复合催化剂上Nb₂O₅特征峰与单组分Nb₂O₅相比明显向低波数偏移, 表明Nb₂O₅和(Ce,Cr)_xO₂之间存在较强的相互作用。N₂吸脱附表征结果显示, y(Ce,Cr)_xO₂/Nb₂O₅为介孔结构, 其织构性质变化与催化活性之间无直接联系。SEM照片显示, 对于复合催化剂, (Ce,Cr)_xO₂颗粒高度分散在片状Nb₂O₅表面, 二者的适当复合有利于其紧密接触并增强相互作用, 进而充分发挥协同催化效应。

NH₃-TPD结果显示, 单组分Nb₂O₅具有最多的强酸中心数量和较高的酸强度, 随着(Ce,Cr)_xO₂含量增加, 强酸和总酸中心数量以及强/弱酸中心数量比值均逐渐减小。H₂-TPR结果显示, Nb₂O₅的氧化能力明显弱于(Ce,Cr)_xO₂, 随着质量比y值增大, Nb₂O₅的δ峰向低温方向移动, 并与(Ce,Cr)_xO₂的γ峰发生重叠, 表明在两者界面处存在Nb^{m+}-O-Ceⁿ⁺强相互作用, γ+δ峰的峰面积先增大后减小的变化趋势, 其中0.25(Ce,Cr)_xO₂/Nb₂O₅的γ+δ峰面积最大。此外, 复合催化剂中Cr⁶⁺物种的α峰面积逐渐增加, 表明强氧化性的Cr⁶⁺物种含量逐渐增大。酸性中心与氧化中心各自单一方向的变化趋势与催化降解性能先增后减的变化趋势并不一致, 表明二者之间的协同催化效应起着重要作用。

综上, 与单组分(Ce,Cr)_xO₂和Nb₂O₅相比, y(Ce,Cr)_xO₂/Nb₂O₅催化剂对DCE的本征催化降解活性显著提高,

0.25(Ce,Cr)_xO₂/Nb₂O₅催化剂显示出最佳性能. 催化剂酸性中心与氧化中心之间存在显著的协同催化效应: 酸性中心有利于DCE的吸附和活化以及C–Cl键断裂得到质子化C₂H₃Cl; 氧化中心则有利于C₂H₃Cl的深度氧化. 合适的(Ce,Cr)_xO₂/Nb₂O₅比有利于(Ce,Cr)_xO₂颗粒在Nb₂O₅表面高度分散, 促进酸性中心与氧化中心之间的协同催化效应, 从而显著提高(Ce,Cr)_xO₂/Nb₂O₅复合催化剂的催化降解性能.

关键词: 1,2-二氯乙烷; 深度氧化; 复合氧化物; 五氧化二铌; 协同催化效应

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