Enhanced catalytic activity and stability of Ce doping on Cr supported HZSM-5 catalysts for deep oxidation of chlorinated volatile organic compounds

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HIGHLIGHTS

- Catalysts containing acidity and oxidizability are prepared by impregnation method.
- Formation of Ce–Cr mixed oxides is beneficial to stabilizing active components.
- Carbon deposition and chlorine adsorption are the main factors for deactivation.
- 9%Cr–12%CeO$_2$/HZSM-5 shows preferable activity and stability for destruction of CVOCs.

ABSTRACT

The CeO$_2$ or/and Cr$_2$O$_3$ modified HZSM-5 zeolite (molar ratio SiO$_2$/Al$_2$O$_3 = 22$) catalysts were prepared by impregnation method and investigated in the catalytic behavior for decomposition of 1,2-dichloroethane (DCE), dichloromethane (DCM) and trichloroethylene (TCE), as well as the durability during 100 h exposure to DCE. The results indicate that 9%Cr–12%CeO$_2$/HZSM-5 exhibits the best catalytic activity and durability for the degradation of CVOCs. The interaction between CeO$_2$ and Cr$_2$O$_3$ increases the amount of Cr$^{6+}$ species with stronger oxidation ability and promotes the mobility of active oxygen species in the modified HZSM-5 catalyst, which is benefit for the deeper oxidation of the intermediates produced in the destruction process of CVOCs and improves the resistance to coke deposit. While the synergy between CeO$_2$ or/and Cr$_2$O$_3$ and HZSM-5 zeolite can promote the dehydrochlorination of CVOCs as well as the formation of suitable strength and density ratio of strong and weak acidity, which is also in favor of improving the ability for the catalytic degradation of CVOCs.

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1. Introduction

Chlorinated volatile organic compounds (CVOCs) consist of a wide range of relatively low molecular-weight compounds and are emitted into the atmosphere from lots of industrial operations [1]. Such compounds are well known for their distinct toxicity, high inertness and long-term persistence in the environment [2]. So developing effective methods for safe disposal or/and conversion of these harmful compounds to more environmentally benign alternatives has become an important challenge. Among all the "end-of-pipe" technologies for CVOCs elimination, catalytic oxidation is an interesting one, since the dilute contaminant (<1000 ppm) can be removed from effluents efficiently and economically, mainly due to its low operating temperature (300–550 °C), high activity and high selectivity [3–5].

Among all the catalysts studied in the past few years, much more attention has been given to zeolite catalysts, mainly due to their special three-dimensional channel structure, shape-selective catalyzing effects, high internal surface area, good thermal stability and large ion-exchange capacity which allows the easily modification of the acid properties on the surface. It has been reported that H-type zeolites, such as H-Y, H-ZSM-5, H-MOR and H-BETA, display good catalytic activity for CVOCs destruction [6–10]. And certain zeolites (such as H-ZSM-5) are particularly resistant to structural collapse under extreme conditions. However, certain deactivation is observed due to their strong acidity, which can promote coke formation [11–13]. Previous studies have also indicated that transition metals modified zeolite catalysts exhibit good catalytic activity for the destruction of CVOCs, though they are relatively less active than noble metal modified zeolite catalysts [14–18]. At the same time, transition metal oxides are found to be more suitable for the chemical resistance to Cl-poisoning than noble metal [19,20]. Particularly, Cr$_2$O$_3$ represents one of the highest catalytic activity, its temperature for total conversion of TCE is lower than...
350 °C. However, when used as single component, the loss of active sites or the formation of volatile species (such as CoCl2 and CrO3Cl2) at low temperature may cause the deactivation of these transition metal oxides in a certain degree, which may restrict the application of transition metal oxides when used alone [19–21].

Recent years have given considerable attention to CeO2-based mixed oxides for the decomposition of non-chlorinated VOCs and CVCs, since CeO2 can undergo a rapid and reversible redox cycle at relatively low temperature, due to its high oxygen ion mobility in the solid solution from bulk to the surface and vice versa [22–29]. However, as far as we can see, less consideration has been given to investigate the suitability of CeO2 modified zeolite catalysts for CVCs destruction [30]. In our previous work, we have found that CeO2 modified USY zeolite (12.5 wt.% loading for CeO2) can enhance the process of DCE dehydrochlorination to form C2H4Cl2, promote the further oxidation of C2H4Cl and improve the selectivity to HCl and CO2 [31–33]. Compared with the macroporous USY zeolite, the shape-selectivity combined with relatively high stability towards coke formation due to the special three-dimensional intersectional channels and proper acidity make HZSM-5 and modified HZSM-5 as a promising catalyst for catalytic oxidation of CVCs.

The scope of this paper is to investigate the catalytic performance and the mechanism for deactivation of CeO2 or/and CrOx modified HZSM-5 catalysts for oxidative destruction of CVCs. It focuses on evaluating the influence of the interaction between CeO2 and CrOx species, as well as the synergy between CeO2–CrOx and HZSM-5 zeolite, on the activity, selectivity and stability for catalytic oxidation of DCE, DCM and TCE under excess of air, since these model compounds are well known to be present simultaneously in various industrial exhaust gases.

2. Experimental

2.1. Catalysts preparation

The molar ratio of SiO2/Al2O3 for HZSM-5 zeolite is 22 (supplied by Fuxu zeolite Corp., China). The catalysts signed as 9%Cr/HZSM-5, 12% CeO2/HZSM-5 and 9%Cr–12%CeO2/HZSM-5 were prepared by impregnating the HZSM-5 zeolite with Ce(NO3)3·6H2O (AR, 98.0%) or/and Cr(NO3)3·6H2O (AR, 98.0%) solution. The loadings of Cr and CeO2 are 9 wt.% and 12 wt.% for the 9%Cr–12%CeO2/HZSM-5 catalyst, respectively. All the impregnated catalysts were dried at 110 °C for 2 h and then calcined in air at 550 °C for 2 h. Finally, all the obtained catalysts were pressed into pellets, crushed and sieved to 40–60 meshes. For comparison, 21%Cr/HZSM-5 and 21%CeO2/HZSM-5 catalysts were also prepared by the same method mentioned above.

2.2. Catalysts characterization

The X-ray diffraction (XRD) measurement was performed on an ARL XTRA X-ray Diffractometer (Thermo Electron Corporation, USA), with Cu Kα radiation at 40 kV and 40 mA in a scanning range of 20–80° (2θ).

The textural properties of the catalysts were determined by N2 adsorption and desorption at liquid nitrogen temperature using a Coulter OMNISORP-100 apparatus. All the samples were degassed under vacuum at 200 °C for 2 h before measurement. Specific total surface area was calculated using the Brunauer–Emmett–Teller (BET) equation.

The ammonia temperature-programmed desorption (NH3-TPD) was performed in a quartz fixed-bed micro-reactor equipped with TCD detector. Prior to adsorption of ammonia, the catalyst (about 100 mg) was pretreated in N2 stream (99.99%, 35 mL min−1) at 500 °C for 0.5 h. After being cooled down to 100 °C, the catalyst was exposed to a flow (30 mL/min–1) of 20 vol.% NH3/N2 mixture for 0.5 h, and then treated in a pure N2 flow for 1 h in order to remove the physical adsorption ammonia. Finally, the desorption experiment was carried out in a pure N2 flow (40 mL min−1) from 100 to 600 °C at a heating rate of 10 °C min−1. All these profiles were simulated by Gaussian functions.

The hydrogen temperature-programmed reduction (H2-TPR) was performed in a quartz fixed-bed micro-reactor equipped with TCD detector, using 5 vol.% H2/Ar mixture (40 mL min−1). After the catalysts were pretreated in air at 300 °C for 0.5 h, the reduction experiment was carried out from 50 to 900 °C at a heating rate of 10 °C min−1.

The coke content of the catalysts after long term reaction at 300 °C was measured through a Thermogravimetric Analyzer (TGA, Perkin Elmer Inc., USA). After pretreated in a pure N2 flow (99.99%, 30 mL min−1) at 120 °C for 0.5 h, the catalysts were further heated up to 800 °C at a heating rate of 10 °C min−1 in a mixture flow (60 mL min−1) of 40 vol.% O2/N2.

2.3. Catalytic activity tests

Catalytic activity tests were carried out in a traditional fixed-bed micro-reactor (quartz glass, 6 mm i.d.) at atmospheric pressure. The feed gas composition was: DCE, DCM or TCE (~1000 ppm) with dry air as the balance gas, and the operating condition was GHSV of 15,000 h−1 with a total flow of 75 mL min−1. During the measurement, the reaction temperature was raised from 100 to 540 °C in steps of 20 °C. After stabilized for 1 h at each temperature, the activity measurement was conducted. The gas stream was analyzed on line over a GC equipped with a packed column (OV 101) and a FID detector for analysis of organic compounds. Conversion was calculated using the peak areas of each compound, relative to the one obtained by bypassing the reactor to provide a blank value. CO in the outlet was analyzed by an on-line gas chromatograph equipped with a carbon molecular sieve (TDX-01) column and analyzed by a FID detector. CO was first converted to methane by a methanation reactor. The analysis was calibrated by injecting a known amount of CO2. Mass spectrum (HIDEN QIC-20) was also connected to the setup, to allow on-line and real-time-resolved measurement of those detected intermediates. The concentration of both CO and CO2 was measured when all the organic compounds were destructed (the final products are only CO2, HCl and Cl2), by bubbling the effluent stream through a 0.0125 M NaOH solution for 0.5 h each time [34]. The Cl2 concentration in the bubbled solution was determined by titration with ferrous ammonium sulphate (FAS) using N,N-diethyl-p-phenylenediamine (DPD) as indicator [35], while the concentration of chloride ions was determined by using an ion selective electrode. Each measurement was repeated for four times.

2.4. Stability tests

The durability tests of the catalysts were performed under the following conditions: the catalyst was exposed to the DCE stream ([DCE] = ~1000 ppm, with dry air as the balance gas) at 300 °C and 260 °C for 100 h, respectively, and the total flow was 75 mL min−1 with GHSV = 15,000 h−1.

3. Results and discussion

3.1. Catalytic performance results

3.1.1. The evaluation for catalytic degradation of TCE

The evaluation results for catalytic oxidation of TCE over pure HZSM-5 zeolite and modified HZSM-5 catalysts are shown in
Fig. 1. As shown in Fig. 1(A), TCE cannot be completely converted until the reaction temperature is higher than 482 °C over pure HZSM-5 zeolite, while the homogeneous reaction occurs only above 450 °C and the conversion of TCE is just 85% when the temperature reaches to 550 °C [6]. However, the catalytic activity is obviously enhanced over modified HZSM-5 zeolite catalysts, especially over 9%Cr–12%CeO2/HZSM-5 catalyst, over which the temperature for TCE complete conversion is only 269 °C. On the basis of T90 (temperature at which 90% conversion is attained), the sequence of the catalytic activity for the TCE destruction is as follows: 9%Cr–12%CeO2/HZSM-5 (269 °C) > 9%Cr/HZSM-5 (314 °C) > 21%Cr/HZSM-5 (333 °C) > 21%CeO2/HZSM-5 (339 °C) > 12%CeO2/HZSM-5 (347 °C) > HZSM-5 (482 °C). This result suggests that the strong interaction between Cr2O3 and CeO2 as well as the synergy between Cr2O3–CeO2 and HZSM-5 zeolite on 9%Cr–12%CeO2/HZSM-5 is appreciably in favor of the TCE destruction. As shown in Fig. 1(B), C2Cl4 is the only intermediate observed during TCE decomposition. As to the final products, there are CO2, CO, HCl and CH3Cl. As far as CO and CO2 formation in CVOCs conversion is concerned, a common feature of the formation of CO2 over CO is observed at high conversion levels. The sequence of the peak concentrations and the selectivity of CO for the TCE destruction is as follows: 9%Cr–12%CeO2/HZSM-5 (60 ppm, 3%) < 9%Cr/HZSM-5 (204 ppm, 10%) < 12%CeO2/HZSM-5 (280 ppm, 14%) < HZSM-5 (360 ppm, 18%). Only small amount of CO is detected over 9%Cr–12%CeO2/HZSM-5 catalyst (CO selectivity is 3%), since the total amount of CO2 is 2000 ppm in the gas stream, due to the presence of excess O2 and its strong oxidation ability (see the results of H2–TPR measurement shown below). All these catalysts show high selectivity to HCl (>90%), which is in accordance with reference [6].

Based on the research results in our group and the mechanism of TCE decomposition reported in previous literature [19,36,37], we suggest the mechanism for TCE decomposition over the catalysts is as follows. TCE is firstly adsorbed on the acid sites (such as Lewis sites) of the catalyst, then it reacts with surface hydroxyl groups to generate acyl chloride species, which can be further oxygenated into CO2, HCl, Cl2 and H2O in the presence of active oxygen species. Meanwhile, the intermediate C2Cl4 is formed via the chlorination of TCE in the presence of metal chloride or Cl2 followed by dehydrochlorination. Combining with our research results, we speculate that more OH groups on the surface of the HZSM-5 favor the dehydrochlorination of TCE and the better redox property of Cr2O3–CeO2 mixed oxide (see the results of H2–TPR measurement shown below) enhances the further oxidation of acyl chloride species due to the stronger interaction between Cr2O3 and CeO2. Therefore, 9%Cr–12%CeO2/HZSM-5 catalyst exhibits the best catalytic activity for TCE decomposition.

In the case of the intermediate C2Cl4 production, compared with other catalysts, especially HZSM-5 zeolite, 9%Cr–12%CeO2/HZSM-5 catalyst exhibits smaller Tmax value (temperature at which maximum concentration reaches) of C2Cl4, which may be attributed to the easier chlorination of chromium than that of cerium. Moreover, the better redox property of the catalyst is also beneficial to Cl2 production via the Deacon reaction (2HCl + 1/2O2 → Cl2 + H2O) over 9%Cr–12%CeO2/HZSM-5. Both of the above two factors are in favor of C2Cl4 production. Therefore, a certain amount of C2Cl4 is produced at low temperature range over 9%Cr–12%CeO2/HZSM-5. Furthermore, the large number of active oxygen species with better mobility and the presence of CrOx species especially CrO42- (see the results of H2–TPR measurement shown below) with stronger oxidizability are beneficial to the rapid oxidation of C2Cl4 into CO2 over this catalyst. Thus, only small amount of C2Cl4 is detected over 9%Cr–12%CeO2/HZSM-5 at low temperature.

3.1.2. The evaluation for catalytic degradation of DCM

The results of catalytic activity tests for catalytic oxidation of DCM over pure HZSM-5 zeolite and modified HZSM-5 catalysts are shown in Fig. 2. The homogeneous reaction occurs only above 350 °C and the conversion of DCM is just 50% when the temperature reaches to 500 °C [8]. As presented in Fig. 2(A), the catalytic activity for DCM destruction is much higher over CeO2 or/and Cr2O3 modified HZSM-5 catalysts than that over HZSM-5 and Cr2O3 modified zeolite, suggesting that the synergy between CeO2 or/and Cr2O3 and HZSM-5 zeolite is also beneficial for DCM destruction. The catalytic activity for DCM conversion according to T90 decreases in the order: 9%Cr–12%CeO2/HZSM-5 (306 °C) > 12%CeO2/HZSM-5 (311 °C) > 9%Cr/HZSM-5 (328 °C) > HZSM-5 (334 °C). As shown in Fig. 2(B), only one intermediate (i.e. CH2Cl) is detected in the catalytic degradation process of DCM. Compared with unmodified HZSM-5 zeolite, only small amount of CH2Cl is produced over CeO2 modified HZSM-5 catalyst, while nearly no CH2Cl is detected over Cr2O3 or/and CeO2 modified HZSM-5 catalysts. The results demonstrate that the addition of Cr2O3 together with the interaction between Cr2O3 and CeO2 species inhibits the production of CH2Cl.

Some documents [38–40] have reported that the catalytic degradation mechanism of DCM is similar to that of TCE mentioned above. DCM first reacts with surface OH species of the catalysts to form adsorbed HCHO intermediate, producing HCl at the same time. Then the HCHO is transformed into methoxy group and formate species through disproportionate reaction. Finally, the methoxy group reacts with the HCl to form intermediate CH3Cl, while the formate species are further converted to CO2. With regard to the intermediate CH3Cl, it cannot be produced until a certain
amount of adsorbed formaldehyde species is formed. After CeO₂ species are introduced into HZSM-5 zeolite, T_max of CH₃Cl shifts to lower temperature range and the concentration of CH₃Cl decreases obviously. It is presumed that the presence of CeO₂ species with better oxygen storage/release behavior would promote the formation of methoxy species. Therefore, small amount of CH₃Cl resulted from the reaction between methoxy species and HCl is detec ted over 12%CeO₂/HZSM-5. However, the further oxidation of the formaldehyde and formate species is promoted over 9%Cr–12%CeO₂/HZSM-5 catalyst in the presence of Cr₂O₃ species especially Cr⁶⁺ with stronger oxidation ability, as well as more active oxygen species with better mobility resulted from the interaction between Cr₂O₃ and CeO₂. Therefore, nearly no CH₃Cl is observed over 9%Cr–12%CeO₂/HZSM-5.

3.1.3. The evaluation for catalytic degradation of DCE

The catalytic behavior for decomposition of DCE over these cata lysts is shown in Fig. 3. As presented in Fig. 3 (A), 12%CeO₂/HZSM-5 exhibits improved DCE conversion compared with pure HZSM-5, and the further addition of Cr₂O₃ is beneficial to DCE conversion, while the homogeneous reaction occurs only above 420 °C and the conversion of DCE is 95% when the temperature reaches to 500 °C [6]. It is clear that the 9%Cr–12%CeO₂/HZSM-5 catalyst displays the best ability to promote DCE to form CH₃Cl through dehydrochlorination. The sequence of the catalytic activity for DCE destruction according to the values of T₉₀ is: 9%Cr–12%CeO₂/HZSM-5 (258 °C) > 12%CeO₂/HZSM-5 (267 °C) > 9%Cr/HZSM-5 (273 °C) > HZSM-5 (278 °C). As presented in Fig. 3 (B–E), in the catalytic degradation process of DCE, the main intermediates are CH₂Cl, CH₂HCl, CH₂CHO and CH₂COOH, without producing any high-chlorinated intermediates over the catalysts. Moreover, the concentration of these intermediates over 9%Cr–12%CeO₂/HZSM-5 is obviously smaller than that over other catalysts.

According to previous literatures [41,42], DCE firstly transforms into CH₂HCl via dehydrochlorination of DCE in the presence of LO acid sites at low temperature. Then CH₂HCl is protonized by OH group on the surface of the catalysts to form carbonium ion. After that, this ion is attacked by nucleophilic oxygen species on the surface of the catalysts to form chlorohydrine salt. Then it is further oxygenated into CH₂CHO, CH₂COOH and CO₂. At high temperature, CH₂Cl is also produced from DCE cracking on the strong acid sites. As shown in Fig. 1(B), it starts to exist at relatively low temperature (about 200 °C) over HZSM-5 with strong acidity and increases rapidly when the temperature is higher than 300 °C, while the amount of CH₂Cl decreases obviously over 12%CeO₂/HZSM-5 especially when Cr₂O₃ is further added. It is caused by the reduction of strong acid sites which inhibits the production of CH₃Cl. In addition, the oxidation of CH₃Cl can be promoted over CeO₂ or/and Cr₂O₃ modified HZSM-5 catalysts due to the presence of Cr⁶⁺ with strong oxidation ability as well as CeO₂ species with better oxygen storage/release behavior. The major intermediate CH₃HCl is produced via the dehydrochlorination of DCE on Lewis acidity. Compared with 12%CeO₂/HZSM-5 catalyst, the concentration of CH₃HCl, CH₂CHO and CH₂COOH decreases obviously with T_max evidently shifting to lower temperature over 9%Cr–12%CeO₂/HZSM-5 catalyst, which demonstrates that the synergy between Cr₂O₃–CeO₂ and HZSM-5 zeolite as well as the strong interaction between Cr₂O₃ and CeO₂ species improves the further dehydrochlorination and deeper oxidation of CH₃Cl.

3.2. Catalyst characterization

3.2.1. Texture and structure

The XRD patterns of the HZSM-5 zeolite and modified HZSM-5 catalysts are presented in Fig. 4. From Fig. 4, we can see that the feature diffraction peaks of HZSM-5 appear over all the catalysts studied, which indicates that the loading of Cr₂O₃ or/and CeO₂ has not changed the framework of HZSM-5 zeolite. Additionally, the principal diffraction peaks of CeO₂ (fluorite-structure of CeO₂ at about 28.6°, 33.0°, 47.6° and 56.4°) appear over all the CeO₂ modified HZSM-5 catalysts, revealing the formation of large crystallites of CeO₂. For 9%Cr/HZSM-5 catalyst, there appears the figure diffraction peaks of 33.6°, 36.3° and 54.9° for Cr₂O₃ [43]. However, the signals of the figure diffraction peaks assigned to Cr₂O₃ and CeO₂ are all declined over 9%Cr–12%CeO₂/HZSM-5 catalyst. In addition, the lattice parameters of CeO₂ over 9%Cr–12%CeO₂/HZSM-5 catalysts are decreased from 5.413 Å to 5.393 Å when Cr₂O₃ is added, and this means partial Cr ions enters into the crystal lattice of CeO₂, leading to the decrease of the unit cell of CeO₂, since the radius of the Cr³⁺ (0.52 Å) is smaller than that of Ce⁴⁺ (0.97 Å). Moreover, the dimensions of the CeO₂ particles over 9%Cr–12%CeO₂/HZSM-5 catalysts are also decreased from 6.3 nm to 4.1 nm when Cr₂O₃ is added. The results demonstrate that the interaction between Cr₂O₃ and CeO₂ is in favor of the dispersion of metal oxides on HZSM-5 zeolite, thus, its oxidation ability for the destruction of CVOCs can be improved. Moreover, some of the chromium element may combine with cerium to form Cr–Ce–O mixed oxide, which is beneficial to enhancing the stability of active components.

The BET specific surface areas for the catalysts were also measured. Compared with HZSM-5 zeolite (381.9 m²/g), the BET specific surface areas of modified HZSM-5 catalysts decrease...
obviously, 206.3 m$^2$/g for 9%Cr/HZSM-5, 212.8 m$^2$/g for 9%Cr–12%CeO$_2$/HZSM-5 and 290.9 m$^2$/g for 12%CeO$_2$/HZSM-5, respectively. The decrease of the BET specific surface area is mainly due to that the active species deposit on the external zeolite surface and partial of them enter the pore channel of HZSM-5 zeolite (5.4 × 5.6 Å, similar to the dynamic diameter of benzene molecule, 5.8 Å), thus blocking the pore channel of HZSM-5 zeolite. The specific surface area of 9%Cr/HZSM-5 catalyst decreases much more than that of 12%CeO$_2$/HZSM-5, which may be related to the fact that Cr$^{3+}$ with smaller radius than Ce$^{4+}$/Ce$^{3+}$ can enters the pore channel of HZSM-5 zeolite more easily. The decrease of the specific surface area also demonstrates that the micropore structure of HZSM-5 zeolite could be not changed easily by the method of wet impregnation, corresponding with the result of XRD analysis [18,44]. Combining with the activity for the deep oxidation of CVOCs, it is found that the data of BET specific surface area is not compatible with the order of the catalytic activity, indicating that the BET specific surface area is not the main factor in the process of CVOCs destruction for these modified zeolite catalysts.

### 3.2.2. Acidity property

Fig. 5 shows the NH$_3$-TPD profiles of HZSM-5 zeolite and modified HZSM-5 catalysts, and the data of the acidity distribution of the catalysts is listed in Table 1. As shown in Fig. 5, two distinct desorption peaks (x and y) at above 100 °C are observed over all these catalysts, indicating the existence of both Lewis acidity and Brønsted acidity [45]. Compared with HZSM-5 zeolite, the peak-temperature of peak x slightly moves to lower temperature over the modified HZSM-5 catalysts, indicating that the strength of weak acidity is weakened by CeO$_2$ or/and Cr$_2$O$_3$ addition. However, the strength of strong acidity is not affected evidently by CeO$_2$ or/and Cr$_2$O$_3$ species addition according to the little change in peak-temperature of peak y. From Table 1, the total acidity decreases obviously over the modified HZSM-5 catalysts compared...
with that of the HZSM-5 zeolite, which can be assigned to the covering of acid sites by metal deposit as indicated by the decrease of BET surface area. However, the \( A_d/A_w \) values are lower over the modified HZSM-5 catalysts than that of HZSM-5 zeolite, indicating the addition of CeO\(_2\) or/and Cr\(_2\)O\(_3\) results in obvious reduction of strong acidity. While for the oxidative destruction of CVOCs, both B acid sites and L acid sites play an important role [31]. Combining with the results of catalytic activity tests, it is seen that the catalytic activities of 9%Cr–12%CeO\(_2\)/HZSM-5 for CVOCs destruction are evidently higher than that of other catalysts. It indicates that the synergy between Cr\(_2\)O\(_3\)–CeO\(_2\) and HZSM-5 promotes the dehydrochlorination of CVOCs as well as the suitable strength and density ratio of strong and weak acidity is in-favor of the improvement of the ability for catalytic degradation of CVOCs.

### 3.2.3. Redox property

\( \text{H}_2\)-TPR measurement is widely applied to investigate the reducibility of CeO\(_2\)-based materials. Fig. 6 shows the \( \text{H}_2\)-TPR profiles of HZSM-5 zeolite and modified HZSM-5 catalysts. As shown in Fig. 6, no obvious reduction peaks appear for HZSM-5 zeolite, and three reduction peaks are observed for 12%CeO\(_2\)/HZSM-5, which is ascribed to the reduction of surface, subsurface oxygen and bulk oxygen, respectively [46]. Two peaks are observed for 9%Cr/HZSM-5, which is ascribed to reduction of highly dispersed Cr\(_2\)O\(_3\) species and reduction of Cr\(_2\)O\(_3\) with large particle size, respectively. However, the intensity of reduction peak at low temperature range is evidently increased over 9%Cr–12%CeO\(_2\)/HZSM-5 catalyst and the peak moves to lower temperature, indicating that the interaction between CeO\(_2\) and Cr\(_2\)O\(_3\) improves the mobility of the oxygen species over this catalyst. Previous literatures have also reported that the valence of oxidized forms of Cr is higher than 3+ by chemical analysis, XPS and Raman spectroscopy characterization, since there exists a small amount of active Cr (VI) species on the surface of the alumina supported chromium oxide catalysts [47,48], while no Cr (VI) exists for pure chromium in crystalline and amorphous forms. Therefore, the peak observed at about 336 °C should be assigned to the reduction of a little Cr\(^{6+}\) species in 9%Cr–12%CeO\(_2\)/HZSM-5 catalyst. The percentage of Cr\(^{6+}\) species is about 6% of the total Cr content from the calculation of \( \text{H}_2 \)-consumption. In addition, the intensity of the reduction peak for CeO\(_2\) increases and the peak shift evidently to lower temperature range, which indicates that the interaction between CrO\(_x\) and CeO\(_2\) species also weakens the Ce–O bond and promotes the reduction of CeO\(_2\). According to the results, we suggest that the interaction between CeO\(_2\) and CrO\(_x\) increases the amount of Cr\(^{6+}\) species with stronger oxidation ability and the mobility of active oxygen species in the modified HZSM-5 catalysts, which is benefit for the destruction of the intermediates produced in the oxidation process of CVOCs.

### 3.3. Durability tests for catalytic oxidation of DCE

The durability for catalytic oxidation of DCE over pure HZSM-5 and modified HZSM-5 was investigated for 100 h testing, and the results are presented in Fig. 7. As shown in Fig. 7, under the same given condition (300 °C, 15,000 h\(^{-1}\)), the conversion of DCE decreases apparently over pure HZSM-5 zeolite after 100 h test, falling from 99.3% to 86.7%, and it decreases slightly over 9%Cr/HZSM-5 catalyst. While over 12%CeO\(_2\)/HZSM-5 and 9%Cr–12%CeO\(_2\)/HZSM-5, the conversions maintain at 100% under the same condition. As is well known, a certain part of the catalyst bed may not

### Table 1

The distribution of acidity over pure HZSM-5 and modified HZSM-5 zeolite catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>( A_{\text{strong}} )</th>
<th>( A_{\text{weak}} )</th>
<th>( A_{\text{strong}}/A_{\text{weak}} )</th>
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</thead>
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<tr>
<td>HZSM-5</td>
<td>1514</td>
<td>980</td>
<td>1.58</td>
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<tr>
<td>12%CeO(_2)/HZSM-5</td>
<td>1313</td>
<td>917</td>
<td>1.43</td>
</tr>
<tr>
<td>9%Cr/HZSM-5</td>
<td>1317</td>
<td>843</td>
<td>1.56</td>
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<td>9%Cr–12%CeO(_2)/HZSM-5</td>
<td>1320</td>
<td>899</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Fig. 6. \( \text{H}_2\)-TPR profiles of the HZSM-5 zeolite and modified HZSM-5 catalysts: (a) HZSM-5; (b) 12%CeO\(_2\)/HZSM-5; (c) 9%Cr/HZSM-5; (d) 9%Cr–12%CeO\(_2\)/HZSM-5.
participate in the reaction when the conversion reaches to 100%, since the conversion can still be of 100% but the catalyst has been deactivating a little (for example, coke is formed and blocks the active sites) if there is an excess of active sites and this does not affect the conversion determined. Therefore, we have re-evaluated the durability of the 9%Cr–12%CeO2/HZSM-5 catalyst at 260 °C under relatively lower conversion. As shown in Fig. 7, DCE conversion only drops from 93.8% to 91.0% after 100 h. The results indicate that the modification to the HZSM-5 zeolite evidently enhances the durability of the catalysts during the long term tests. Especially for 9%Cr–12%CeO2/HZSM-5, the interaction between CeO2 and Cr2O3 further improves the durability of the catalyst.

It is well known that the carbon deposition on zeolite maybe the main reason for the declination of activity [13]. The main cause of deactivation for HZSM-5 zeolite appears to be the formation of carbonaceous deposits in the micro pores of the crystals, then growing of coke on the external structure of zeolite crystals that physically blocks the pores and active sites. Fig. 8 shows the O2-TG curves of all the catalysts after 100 h testing at 300 °C. From Fig. 8, we can see that in the range of 350–550 °C, the severe loss of weight is observed over pure HZSM-5 catalyst due to its strong acid sites and poor oxidation ability, and the amount of coke deposition reaches to 4.50 wt.%. Likewise, there is also a little coke deposit formed over 9%Cr/HZSM-5 (0.94 wt.%) and 12%CeO2/HZSM-5 (0.90 wt.%), which indicates that the presence of abundant oxygen species is in favor of the deeper oxidation of DCE into CO2. For 9%Cr–12%CeO2/HZSM-5, little coke deposit is found in the range of 350–550 °C. This result indicates that the coke deposit is evidently inhibited ascribed to the better mobility of oxygen species and the formation of Cr6+ species resulted from the strong interaction between CeO2 and Cr2O3. Therefore, the rather slight coke deposition over modified HZSM-5 catalysts is one of the factors to the good durability during the long time tests. After treated in air flow at 500 °C for 0.5 h, the DCE conversions of these spent catalysts were recovered to the original level. And this also indicates that carbon deposition maybe the main reason for the declination of activity, since the activity of these catalysts can be recovered easily by heated in air. While for 9%Cr/HZSM-5 catalyst, its deactivation may be also related to the formation of a little volatile Cr2O3Cl2 species, which leads to the decrease of catalytic activity owing to the loss of active components [19–21].

On the other hand, the decrease of activity for catalytic oxidation of CVOCs may be also due to the strong adsorption of HCl or and Cl2 produced from the decomposition of CVOCs on the surface of the catalysts, thus blocking the active sites, especially under lower temperature condition [49]. Therefore, the conversion of DCE over 9%Cr–12%CeO2/HZSM-5 catalyst shows the decrease of only 2.8% after 100 h test at 260 °C. However, after treated in air flow at 300 °C for 0.5 h, the activity of this catalyst for the oxidation of DCE is recovered again, probably due to that the Cl species adsorbed on the surface are removed (due to the strong oxidizing property of the Cl6+ species), because the oxygenation temperature of the coke deposit on the catalyst is higher than 350 °C.

It is well known that HCl produced in the process of CVOCs destruction can break the Al–O bond and cause the damage of zeolite’s framework. Thus, the XRD analysis of the catalysts after 100 h tests at 300 °C is carried out in order to determine the change in the zeolite framework. The result reveals that after 100 h test the catalysts maintain almost the same framework as fresh HZSM-5 zeolite, and the crystallinity of the fresh HZSM-5 is 87%, while the crystallinity of the used HZSM-5 and 9%Cr–12%CeO2/HZSM-5 is 79% and 77%, respectively. This result indicates that the HZSM-5 zeolite is suitable for the chemical resistance to the corrosion of gaseous HCl and Cl2, since the stability of its framework is preferable during the 100 h exposure to DCE. This can be related to the low aluminium content of HZSM-5 zeolite [6].

4. Conclusions

The CeO2 or/and Cr2O3 modified HZSM-5 zeolite (molar ratio SiO2/Al2O3 = 22) catalysts were prepared by impregnation method and investigated in terms of deep oxidation of DCE, DCM and TCE under excess air. The results reveal that 9%Cr–12%CeO2/HZSM-5 exhibits the best catalytic activity and stability for all these model compounds studied. Both acidic and redox properties play important roles in the deep oxidation of CVOCs. The interaction between Cr2O3 and CeO2 increases the amount of Cr6+ species with stronger oxidation ability and the mobility of active oxygen species in the modified HZSM-5 catalyst, which is benefit for the destruction of the intermediates produced in the oxidation process of CVOCs. While the synergy between CeO2–Cr2O3 and HZSM-5 zeolite promotes the dehydrochlorination of CVOCs, as well as the formation of suitable strength and density ratio of strong and weak acidity, which is also in favor of the improvement of the ability for the catalytic degradation of CVOCs. Besides, the strong interaction between Cr2O3 and CeO2 species as well as the synergy between Cr2O3–CeO2 and HZSM-5 zeolite over 9%Cr–12%CeO2/HZSM-5 can enhance the stability of active components and improve the resistance to coke deposit along with HCl attack on the catalyst. Therefore, 9%Cr–12%CeO2/HZSM-5 shows the best durability and structure stability during the long term exposure to DCE.