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# Three-dimensionallyorderedmacroporousCr2O3-CeO2:High-performance catalysts for the oxidative removal of trichloroethylene

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Graphical\_abstract



The 3DOM  $xCr_2O_3$ –CeO<sub>2</sub> (*x* is the Cr<sub>2</sub>O<sub>3</sub> weight percentage (wt%)) samples are prepared using the polymethyl methacrylate-templating method. The good catalytic stability and Cl<sup>-</sup>-resistant ability of 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> is associated with the strong interaction between Cr<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>.

#### **Research Highlights**

- ► 3DOM *x*Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> is prepared via the polymethyl methacrylate-templating route.
- ► 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> shows the best catalytic activity for trichloroethylene oxidation.
- ► 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> exhibits good catalytic stability and Cl<sup>-</sup>-resistant ability.
- The strong  $Cr_2O_3$ -CeO<sub>2</sub> interaction is responsible for the good stability.

#### **Abstract:**

Three-dimensionally ordered macroporous (3DOM) CeO<sub>2</sub>, 3DOM Cr<sub>2</sub>O<sub>3</sub>, 3DOM xCr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> (*x* (the weight percentage of Cr<sub>2</sub>O<sub>3</sub>) = 3.5, 5.5, and 8.0 wt%), and 5.5 wt% Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> samples were prepared using the polymethyl methacrylate (PMMA)-templating and incipient wetness impregnation methods, respectively. A number of techniques were used to characterize physicochemical properties of the materials, and their catalytic activities were evaluated for the oxidation of trichloroethylene (TCE). These

samples possessed a good-quality 3DOM structure and a surface area of  $35-47 \text{ m}^2/\text{g}$ . The 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> sample performed the best (the temperature at TCE conversion = 90 % = 255 °C at a space velocity of 20,000 mL/(g h)). Effects of water vapor and carbon dioxide on activity of the 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> sample were also examined. It is observed that partial deactivation induced by H<sub>2</sub>O introduction of the 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> sample was reversible, while that induced by CO<sub>2</sub> addition was irreversible. Based on the activity data and characterization results, it is concluded that the good catalytic activity and thermal stability of 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> was associated with its high adsorbed oxygen species concentration, good low-temperature reducibility, and strong interaction between Cr<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>. We believe that the 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst is promising in the application for oxidative removal of chlorinated volatile organic compounds.

**Keywords:** Three-dimensionally ordered macropore; Ceria; Chromia; Chromia–ceria composite oxide; Trichloroethylene oxidation.

#### **1. Introduction**

Chlorinated volatile organic compounds (CVOCs) are harmful to the environment and human health [1]. Among the CVOCs, dichloromethane, 1,2-dichloroethane, chlorobenzene, and trichloroethylene (TCE) have received much attention due to their high toxicity, stability, and widespread applications in industry. Catalytic oxidation is one of the most effective pathways for the abatement of CVOCs, in which supported noble metals and base metal oxides are the most commonly used catalysts [2–5]. The severe nature of CVOCs

requires the catalysts to show good activity at low temperatures and good stability (resistant to the poisoning of the formed chlorides). Therefore, it is highly desired to develop high-performance and good-stability catalysts for the oxidative removal of CVOCs.

Although supported noble metal (e.g., Pt, Pd, Rh or Ru) catalysts show good activity and high selectivity to CO<sub>2</sub> and HCl in the oxidative destruction of CVOCs, they are expensive and easy to be poisoned by the formed HCl and Cl<sub>2</sub> as well as easily deactivated by carbon deposition [6,7]. For example, Taralunga et al. [8] reported that the 1.2 wt% PtHY catalyst was deactivated within 24 h of on-stream 1,2-dichlorobenzene oxidation and the deactivation was due to the sintering of Pt. After having investigated the Ru-doped CeO<sub>2</sub> catalysts for the combustion of chlorobenzene, Dai et al. [9] found that the Ru-CeO<sub>2</sub> catalysts showed excellent performance ( $T_{90\%} < 250$  °C) and good stability (no significant deactivation within 80 h of on-stream reaction at 275 °C), which was ascribed to the rapid removal of the inorganic chlorine species adsorbed on the active sites via the Deacon process catalyzed by the RuO<sub>2</sub> component.

Base metal oxides catalysts have been proposed as potential substitutes for noble metal-based catalysts. Although base metal oxides are usually less active than noble metals, they possess excellent redox properties [10] and are more resistant to deactivation. For example, Zuo et al. [11] found that the CrCe (6 : 1)/Ti-PILC catalyst showed higher activity (complete conversion of low-concentration chlorobenzene was achieved at ca. 250 °C) than the Na-montmorillonite-supported catalysts, which was due to the fact that Ti-PILC exhibited a significantly larger basal space and higher surface area and pore volume as compared with Na-montmorillonite. Wang et al. [12] pointed out that the good performance

of  $Ce_{0.5}Ti_{0.5}O_2$  for 1,2-dichlorobenzene combustion has the highest apparent activity with T<sub>90%</sub> about 375 °C, was due to the incorporation of Ti distorted the crystal structure and thus increased greatly the acidity and the oxygen mobility at high temperature. Meanwhile, Ti improved the stability of  $Ce_{1-x}Ti_xO_2$  catalysts through retarding the exchange of Cl for basic lattice oxygen and hydroxyl groups. Among base metal oxide catalysts, CeO<sub>2</sub>-based catalysts (e.g., CeO<sub>2</sub>–MnO<sub>x</sub> [13–15], CeO<sub>2</sub>–ZrO<sub>2</sub> [16–19], and Ce<sub>x</sub>Pr<sub>1-x</sub>O<sub>2</sub> [20]) have been extensively investigated due to their outstanding redox properties, oxygen storage capacity, cheapness, environment benign nature, considerable oxidative activity in CVOCs oxidation, and good resistance to Cl-poisoning. Among the Ce-based catalysts, pure ceria exhibited fairly high catalytic activity for CVOCs oxidation [21,22]. Porous ceria with rich porosity, high surface area, narrow pore-size distribution, and good reducibility is expected to possess improved physicochemical properties [23-27]. In addition, chromium-based catalysts exhibited high activity for the abatement of CVOCs [28-30]. Nevertheless, the use of this type of catalysts tends to be restricted due to formation of extremely toxic residues (e.g., chromium oxychloride) at high temperatures and volatilization of the active phase [31,32].

Although modified Cr-based catalysts have been applied to remove the CVOCs, there are still some aspects to be improved, such as the type and structure of the catalyst support and the optimized loading of Cr. Compared with the nonporous catalysts, the three-dimensionally ordered macroporous (3DOM) catalysts exhibit better performance owing to their higher surface areas and easy diffusion properties. Previously, our group adopted the polymethyl methacrylate (PMMA)-templating and polyvinyl alcohol-protected

reduction strategies to generate a series of 3DOM-structured catalytic materials [33–35], and observed that most of them performed well in the oxidation of VOCs. In this work, we report the preparation of 3DOM  $xCr_2O_3$ –CeO<sub>2</sub> and 3DOM CeO<sub>2</sub>-supported Cr<sub>2</sub>O<sub>3</sub> using the PMMA-templating and incipient wetness impregnation methods, respectively, and investigated their catalytic properties for the oxidative removal of TCE. It is found that the 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> sample showed good activity and stability for the addressed reaction.

#### 2. Experimental

#### 2.1. Catalyst preparation

Well-arrayed colloidal crystal PMMA microspheres with an average diameter of 300 nm were synthesized according to the procedure described elsewhere [36]. The 3DOM  $xCr_2O_3$ -CeO<sub>2</sub> (*x* is the weight percentage (wt%) of Cr<sub>2</sub>O<sub>3</sub>) samples were prepared using the PMMA-templating method [27]. In a typical preparation, 1.0 g of polyethylene glycol (PEG)-10000, 4.34 g of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, and 0, 0.13, 0.20, and 0.30 g of Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were dissolved in 10.0 g of ethanol aqueous solution (40 wt%) at room temperature (RT) under stirring for 4 h. After dissolution, 2.0 g of the PMMA template was soaked in the above transparent solution for 6 h. After being filtered and dried at RT for 36 h, the obtained powders were calcined in a N<sub>2</sub> flow of 200 mL/min at a ramp of 1 °C/min from RT to 300 °C and kept at this temperature for 3 h, then cooled to 50 °C under the same atmosphere, and finally in an air flow of 200 mL/min at a ramp of 1 °C/min from RT to 600 °C and maintained at this temperature for 5 h, thus obtaining the 3DOM  $xCr_2O_3$ -CeO<sub>2</sub> (x = 0, 3.5, 5.5, and 8.0) samples.

For comparison purposes, 3DOM  $Cr_2O_3$  was also prepared using the above same method with  $Cr(NO_3)_3 \cdot 9H_2O$  as chromium source. The 5.5 $Cr_2O_3/3DOM$  CeO<sub>2</sub> sample was prepared via the incipient wetness impregnation route. In a typical preparation, 0.50 g of 3DOM CeO<sub>2</sub> was impregnated with 5.0 mL of Cr(NO<sub>3</sub>)<sub>3</sub>-ethanol aqueous solution (0.015 mol/mL) for 30 min. After that, the mixture was dried at 80 °C for 12 h, and then calcined in an air flow of 200 mL/min at a ramp of 1 °C/min from RT to 600 °C and maintained at this temperature for 5 h.

#### 2.2. Catalyst characterization

Physicochemical properties of the samples were characterized by means of techniques, such as inductively coupled plasma–atomic emission spectroscopic (ICP–AES), X-ray diffraction (XRD), laser Raman, scanning electron microscopy (SEM), transmission electron microscopy (TEM), high angle annular dark field and scanning transmission electron microscopy (HAADF–STEM), N<sub>2</sub> adsorption–desorption (BET), X-ray photoelectron spectroscopy (XPS), hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR), and NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>-TPD). The detailed characterization procedures are described in the Supplementary material.

#### 2.3. Catalytic activity evaluation

The catalytic activities of the samples were evaluated in a continuous flow fixed-bed quartz microreactor (i.d. = 6 mm). To minimize the effect of hot spots, 50 mg of the sample (40–60 mesh) was mixed with 0.25 g of quartz sands (40–60 mesh). Prior to the test, the sample was treated in air (30 mL/min) at 350 °C for 1 h. After being cooled to a given temperature, the reactant gas mixture containing trichloroethylene (TCE) was passed

through the catalyst bed. The total flow rate of the reactant mixture (750 ppm TCE + 20 vol% O<sub>2</sub> + N<sub>2</sub> (balance)) was 16.7 mL/min and the space velocity (SV) was ca. 20,000 mL/(g h). After the reaction was stabilized for 1 h at a certain temperature, the reactants and products were online analyzed by a gas chromatograph (GC-7890B, Agilent) equipped with a flame ionization detector (FID) and a TCD, using a Agilent 19091J-413 HP-5 (30 m in length) and G3591-81141 (silica gel), G3591-81142 (silica gel), and G3591-81022 (molsieve 5A, 2.44 m in length of each packing column). The TCD was used to analyze the CO<sub>2</sub> and CO concentrations, whereas the FID used to analyze the concentrations of the organic compounds. The TCE conversion is defined as  $(c_{inlet}-c_{outlet})/c_{inlet} \times 100$  %, where the c<sub>inlet</sub> and c<sub>outlet</sub> are the inlet and outlet TCE concentrations in the feed stream, respectively. In the case of water vapor introduction, 3.0 or 5.0 vol% H<sub>2</sub>O was introduced by passing the feed stream through a water saturator at 23 and 34 °C, respectively. In the case of CO<sub>2</sub> addition, 5.0 or 10 vol% CO<sub>2</sub> was introduced from a CO<sub>2</sub> cylinder with N<sub>2</sub> as balance gas. The balance of carbon throughout the catalytic system was estimated to be  $99.5 \pm 1.5$  %. The evolution of possible intermediates and products was checked online by the Agilent GC-MS equipment.

Selectivities to HCl and Cl<sub>2</sub> were measured by bubbling the outlet gas mixture through a NaOH aqueous solution (12.5 mmol/L) for 0.5 h each time. The Cl<sub>2</sub> concentration in the bubbled solution was determined by chemical titration with ferrous ammonium sulfate using *N*,*N*-diethyl-*p*-phenylenediamine as indicator, and the Cl<sup>-</sup> concentration was measured using an ion selective electrode.

#### **3. Results and discussion**

#### 3.1. Crystal phase, morphology, pore structure, and surface area

Fig. 1 shows the XRD patterns of the 3DOM CeO<sub>2</sub>, 3DOM Cr<sub>2</sub>O<sub>3</sub>, 3DOM xCr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> samples. According to the XRD pattern (JCPDS PDF# 81-0792) of the standard ceria sample, we deduce that the CeO<sub>2</sub> in the 3DOM CeO<sub>2</sub>, 3DOM xCr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> samples possessed a cubic fluorite-type crystal structure. By comparing the XRD pattern (JCPDS PDF# 84-1616) of the standard chromia sample, one can realize that 3DOM Cr<sub>2</sub>O<sub>3</sub> was of a rhombohedral Cr<sub>2</sub>O<sub>3</sub> phase. All of the Bragg diffraction peaks due to cubic CeO<sub>2</sub> and rhombohedral Cr<sub>2</sub>O<sub>3</sub> can be well indexed, as indicated in Fig. 1e and f. Weak diffraction signals assignable to the Cr<sub>2</sub>O<sub>3</sub> phase were detected in the 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> samples (Fig. 1b, c, and d); however, no diffraction signals of the Cr<sub>2</sub>O<sub>3</sub> phase were recorded in the 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> sample (Fig. 1a), a result possibly due to the low Cr<sub>2</sub>O<sub>3</sub> content and good dispersion in this sample.

Raman spectra of the fluorite-type structures are sensitive to the crystalline symmetry and related to the lattice oxygen vibrations. In order to further investigate the phase structures of the samples, we recorded their Raman spectra, as shown in Fig. 2. The characteristic Raman bands of 3DOM  $Cr_2O_3$  were observed at 301, 383, 503, 533, and 590 cm<sup>-1</sup>. The most intense Raman band at 533 cm<sup>-1</sup> was assigned to the A<sub>1g</sub> symmetry, the bands at 301 and 383 cm<sup>-1</sup> was due to the E<sub>g</sub> symmetry, and the band with a medium intensity at 503 cm<sup>-1</sup> and the band at 590 cm<sup>-1</sup> were assigned to the Cr–O stretching vibration (F<sub>2g</sub> symmetry) [37–41]. For the 3DOM CeO<sub>2</sub>, 3DOM *x*Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> samples, the Raman spectra were dominated by a strong band

centered at 449 cm<sup>-1</sup> and two less prominent broad bands centered at 320 and 580 cm<sup>-1</sup>. The band at 449 cm<sup>-1</sup> was assigned to the defect space of oxygen vacancy in the CeO<sub>2</sub> lattice, the band at 580 cm<sup>-1</sup> was ascribed to the non-degenerate LO mode of CeO<sub>2</sub> due to the relaxation of symmetry rules (which was connected with the oxygen vacancies, due to the presence of Ce<sup>3+</sup> ions in CeO<sub>2</sub> lattice), and the band at 320 cm<sup>-1</sup> was attributed to the displacement of oxygen atoms from their ideal fluorite lattice positions to the tetragonal positions (also suggesting the existence of a defect structure). With increasing the Cr<sub>2</sub>O<sub>3</sub> content, the band at 449 cm<sup>-1</sup> was weakened, indicating the decrease of the cubic fluorite-type phase (*c*-phase); however, the band at 580 cm<sup>-1</sup> increased in intensity, which indicates the increase of oxygen vacancy concentration [42–44]. According to the literature [44,45], oxygen vacancies could favor the redox reactions and thus promote deep oxidation of CVOCs over the catalysts.

Fig. 3 shows the SEM images of the samples. It can be clearly observed that the 3DOM  $CeO_2$  and 3DOM  $Cr_2O_3$  samples displayed a high-quality 3DOM architecture (Fig. 3a and b); with the doping or loading of  $Cr_2O_3$ , the 3DOM structure of the sample slightly decreased in quality (Fig. 3c–i). The periodic voids in the long-range ordered structure were interconnected through open windows with a size of 120–160 nm. The TEM images (Fig. 4) of the samples confirm the formation of good-quality 3DOM structures. In order to further examine the homogeneous dispersion of  $Cr_2O_3$  and  $CeO_2$ , we recorded the HAADF–STEM and EDS elemental mapping images (Fig. 5) of the 3DOM 5.5 $Cr_2O_3$ –CeO<sub>2</sub> sample. Obviously, the  $Cr_2O_3$  and CeO<sub>2</sub> were uniformly distributed in the 3DOM 5.5 $Cr_2O_3$ –CeO<sub>2</sub> sample.

Fig. 6 shows the N<sub>2</sub> adsorption-desorption isotherms and pore-size distributions of the 3DOM CeO<sub>2</sub>, 3DOM Cr<sub>2</sub>O<sub>3</sub>, 3DOM xCr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> samples. Each sample exhibited a type II isotherm with an H3 hysteresis loop in the relative pressure  $(p/p_0)$  range of 0.8–1.0. There was also a small H2 type hysteresis loop in the  $p/p_0$  range of 0.2–0.8. The H3 hysteresis loop (which did not clearly show any adsorption plateau at  $p/p_0$ close to unity) was related to the existence of slit-shaped pores in the materials, which was indicative of macropore formation [26]. The low-pressure portion of the almost linear middle section of each isotherm (which could be attributed to the multilayer adsorption) also suggests formation of macropores [46]. The H2 hysteresis loop in the  $p/p_0$  range of 0.2–0.8 (which was linkable to the capillary condensation taking place in mesopores) indicates the presence of mesopores in the skeleton of 3DOM CeO<sub>2</sub> [26,46,47]. In the pore-size distribution, of each sample, there were mesopores (2-10 nm) and pores scattered from 20 to140 nm (Table 1). Surface areas (40.3–43.6 m<sup>2</sup>/g) of the 3DOM  $xCr_2O_3$ –CeO<sub>2</sub> samples were slightly lower than that  $(47.3 \text{ m}^2/\text{g})$  of the 3DOM CeO<sub>2</sub> sample, but higher than that  $(34.9 \text{ m}^2/\text{g})$  of the 3DOM Cr<sub>2</sub>O<sub>3</sub> sample (Table 1). It should be noted that the 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> sample displayed the lowest surface area (27.6  $m^2/g$ ), a result possibly due to the blocking of macropores by part of the Cr<sub>2</sub>O<sub>3</sub> entities. All of the samples possessed a pore volume of 0.210-0.233 cm<sup>3</sup>/g.

#### 3.2. Surface element composition, metal oxidation, and oxygen species

XPS is an effective technique to investigate the surface element compositions, metal oxidation states, and adsorbed oxygen species of a catalyst. The Ce 3d, Cr  $2p_{3/2}$ , O 1s XPS spectra of the samples are illustrated in Fig. 7. There were two sets of signals,

corresponding to the Ce 3d<sub>3/2</sub> and Ce 3d<sub>5/2</sub> states; Ce 3d spectrum of each sample contained the  $3d_{3/2}$  feature at binding energy (BE) = 901.4, 902.9, 908.0, and 917.1 eV and the  $3d_{5/2}$ feature at BE = 882.8, 884.8, 889.5, and 898.8 eV (Fig. 7A). The signals at BE = 884.8 and 902.9 eV were assigned to the surface  $Ce^{3+}$  species, whereas the others were ascribed to the surface Ce<sup>4+</sup> species [26,35,48]. This result suggests that cerium on the surface of each sample existed in a mixed oxidation state of  $Ce^{3+}$  and  $Ce^{4+}$ . The discrepancy in peak area reflected the different  $Ce^{3+}/Ce^{4+}$  molar ratios on the surface of the mixed oxide samples. The existence of  $Ce^{3+}$  species indicates formation of oxygen vacancies in the CeO<sub>2</sub> lattice, which was beneficial for the generation of active oxygen species [35,49]. As shown in Fig. 7B, the asymmetric O 1s XPS signal could be decomposed to three components at BE = 529.6, 513.3, and 533.7 eV, ascribable to the surface lattice oxygen (O<sub>latt</sub>), adsorbed oxygen  $(O_{ads}, e.g., O_2^-, O_2^{2-} \text{ or } O^-)$ , and carbonate or adsorbed water species [27,35], respectively. The  $O_{ads}/O_{latt}$  molar ratio decreased in the order of 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> (0.51) > 3DOM  $8.0Cr_2O_3$ -CeO<sub>2</sub> (0.45) > 3DOM  $3.5Cr_2O_3$ -CeO<sub>2</sub> (0.41) >  $5.5Cr_2O_3$ /3DOM CeO<sub>2</sub> (0.40) >  $3DOM Cr_2O_3$  (0.39) >  $3DOM CeO_2$  (0.38), and the  $3DOM 5.5Cr_2O_3$ -CeO<sub>2</sub> sample possessed the highest Oads/Olatt molar ratio (Table 2). Since the surface adsorbed oxygen species could play an important role in deep oxidation of organics [33,35], it is expected that 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> sample would show good catalytic activity for TCE combustion. The Cr 2p<sub>3/2</sub> XPS spectrum of each sample could be decomposed into three components at BE = 576.1, 576.6, and 578.5 eV (Fig. 7C), attributable to the surface  $Cr(OH)_3$  or  $Cr_2O_3$  [50],  $Cr^{3+}$  [51,52], and  $Cr^{6+}$  [53,54] species, respectively. The  $Cr^{6+}/Cr^{3+}$ molar ratio increased from 0.26 to 0.35 with the rise in Cr<sub>2</sub>O<sub>3</sub> doping from 3.5 to 8.0 wt%

(Table 2). It should be mentioned that the surface  $Ce^{4+}$  species might facilitate  $Cr^{3+}$ reduction at the  $Cr_2O_3$ -CeO<sub>2</sub> interfaces via  $3Ce^{4+} + Cr^{3+} \rightarrow 3Ce^{3+} + Cr^{6+}$ , resulting in increases in  $Ce^{3+}$  and  $Cr^{6+}$  species concentrations. According to the literature [32,55],  $Cr^{6+}$ species exhibited a strong oxidizing ability and the presence of  $Cr^{6+}$  species would be beneficial for deep oxidation of CVOCs.

#### 3.3. Low-temperature reducibility

H<sub>2</sub>-TPR technique was used to investigate the reducibility of 3DOM CeO<sub>2</sub>, 3DOM Cr<sub>2</sub>O<sub>3</sub>, 3DOM xCr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> samples within 100-800 °C, and their profiles are illustrated in Fig. 8A. For the 3DOM CeO<sub>2</sub> sample, there were two peaks at 465 and 698 °C, in which the former was probably associated with the outmost layer reduction of  $Ce^{4+}$  to  $Ce^{3+}$  and adsorbed oxygen species, whereas the latter was due to the reduction of the inner  $Ce^{4+}$  to  $Ce^{3+}$  and lattice oxygen species [35]. After introduction of  $Cr_2O_3$  to  $CeO_2$ , the initial reduction peak shifted to a lower temperature, indicating that the reducibility of the sample was improved after Cr<sub>2</sub>O<sub>3</sub> doping. Comparing to the 3DOM CeO<sub>2</sub> sample, the 3DOM xCr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> samples were more reducible at lower temperatures. The reduction peaks of the 3DOM  $xCr_2O_3$ -CeO<sub>2</sub> samples shifted to lower temperatures, with the 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> sample possessing the lowest reduction temperature of 284 °C. By quantitatively analyzing the reduction peaks in the H<sub>2</sub>-TPR profiles, we can obtain the H<sub>2</sub> consumption of the 3DOM CeO<sub>2</sub>, 3DOM Cr<sub>2</sub>O<sub>3</sub>, 3DOM xCr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> samples, as summarized in Table 2. Apparently, the H<sub>2</sub> consumption of 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> was higher than that of 3DOM CeO<sub>2</sub>. Generally speaking, the initial (where less than 25 % oxygen in the sample is consumed for

the first reduction peak) H<sub>2</sub> consumption rate can be used to evaluate the low-temperature reducibility of a sample [56], and the results are shown in Fig. 8B. It is observed that the initial H<sub>2</sub> consumption rate (i.e., low-temperature reducibility) decreased in the order of 3DOM  $5.5Cr_2O_3$ -CeO<sub>2</sub> > 3DOM  $8.0Cr_2O_3$ -CeO<sub>2</sub> > 3DOM  $3.5Cr_2O_3$ -CeO<sub>2</sub> > 3DOM  $Cr_2O_3$ -Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>

#### 3.4. Catalytic performance

Fig. 9A shows the catalytic activities of the 3DOM CeO<sub>2</sub>, 3DOM Cr<sub>2</sub>O<sub>3</sub>, 3DOM  $xCr_2O_3$ –CeO<sub>2</sub>, and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> samples for TCE combustion. TCE could not be completely oxidized over 3DOM CeO<sub>2</sub>, and only 31 % TCE conversion was obtained at 350 °C. After the doping of Cr<sub>2</sub>O<sub>3</sub>, however, catalytic activity increased obviously. The 3DOM  $xCr_2O_3$ –CeO<sub>2</sub> samples performed much better than the 3DOM CeO<sub>2</sub> or 3DOM Cr<sub>2</sub>O<sub>3</sub> sample. It is convenient to compare catalytic activities of the samples using the reaction temperatures  $T_{10\%}$ ,  $T_{50\%}$ , and  $T_{90\%}$  (corresponding to TCE conversion = 10, 50, and 90 %), as summarized in Table 3. Apparently, the catalytic activity decreased in the sequence of 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> > 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> > 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> > 3DOM CeO<sub>2</sub> > 3DOM CeO<sub>2</sub> = 214 °C, and  $T_{90\%}$  = 255 °C at SV = 20,000 mL/(g h)). The sequence in catalytic activity of these samples was basically agreeable with those in O<sub>ads</sub>/O<sub>latt</sub> molar ratio and low-temperature reducibility.

Previous works have reported that the oxidation of CVOCs over LaMn<sub>1+x</sub>O<sub>3</sub> [57], Cr<sub>2</sub>O<sub>3</sub> [58], Ru/Al<sub>2</sub>O<sub>3</sub> [59], and Mn<sub>x</sub>Ce<sub>1-x</sub>O<sub>2</sub>/HZSM-5 [60] obeyed a reaction mechanism of a first-order toward CVOC concentration and a zero-order toward O<sub>2</sub> concentration.

Therefore, it is reasonably supposed that TCE oxidation in the presence of excess oxygen (TCE/O<sub>2</sub> molar ratio = 1/1090) would follow a first-order reaction mechanism with respect to TCE concentration (*c*):  $r = -kc = (-A \exp(-E_a/RT)) c$ , where *r* is the reaction rate (mol/s), *k* is the rate constant (s<sup>-1</sup>), *A* is the pre-exponential factor, and *E*<sub>a</sub> is the apparent activation energy (kJ/mol). It is well known that the lower the apparent activation energy (kJ/mol). It is well known that the lower the apparent activation energy (*E*<sub>a</sub>), the easier the complete oxidation of an organic compound over the catalyst, and hence the better is the catalytic performance. The discrepancy in *E*<sub>a</sub> of the samples could reflect their different catalytic activities. Fig. 9B shows the Arrhenius plots for the oxidation of TCE conversion <20% over the samples and their *E*<sub>a</sub> values are summarized in Table 3. Apparently, the *E*<sub>a</sub> increased in the sequence of 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> < 3DOM Cr<sub>2</sub>O<sub>3</sub> < 3DOM CeO<sub>2</sub>, in rough agreement with the order in reaction rate. The 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> sample exhibited the lowest *E*<sub>a</sub> (81 kJ/mol).

In the catalytic elimination of CVOCs, there might be some by-products. We detected the product mixture of TCE oxidation, and the results are shown in Fig. 10. Within the detection limits of TCD and FID, C<sub>2</sub>Cl<sub>4</sub> was the only by-product detected in the outlet gas mixture during the TCE oxidation process. Over the 3DOM CeO<sub>2</sub> sample, a low concentration of C<sub>2</sub>Cl<sub>4</sub> at  $T_{\text{max}}$  (temperature at which the maximum concentration reached) was detected and the maximum concentration was 30 ppm at  $T_{\text{max}} = 330$  °C; over the 3DOM xCr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> samples, however, very low concentrations of the by-products were detected and the maximum concentrations were < 60 ppm. Moreover, the amount of by-products decreased with the rise in Cr<sub>2</sub>O<sub>3</sub> doping and

was lower than 100 ppm over the Cr<sub>2</sub>O<sub>3</sub>-containing samples. Fig. S1 shows the NH<sub>3</sub>-TPD profiles of the samples, and the relative amounts  $(A_{\text{strong}}/A_{\text{weak}})$  of strong and weak acid sites are summarized in Table S2. Obviously, the doping of Cr<sub>2</sub>O<sub>3</sub> promoted formation of the strong acidic sites, and the amount of strong acidic sites in 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> was more than that in 3DOM CeO<sub>2</sub>, suggesting that Cr<sub>2</sub>O<sub>3</sub> doping could enhance the acidity of the sample. The basic sites in the samples might be responsible for formation of the by-products. The low amounts of the by-products formed over the 3DOM xCr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> samples were related to the weak base strength (i.e., the strong acid sites). CeO<sub>2</sub> possesses unique  $Ce^{4+}/Ce^{3+}$  redox property, strong interactions with metals or metal oxides, and good ability for dissociating C-Cl bonds. However, deactivation due to strong adsorption of Cl species produced during CVOCs oxidation processes, high activity in chlorination, and low resistance to water of CeO<sub>2</sub> limit its wide industrial applications. It is well known that Cl tends to be adsorbed on oxygen vacancies of CeO<sub>2</sub>. The doping of Cr<sub>2</sub>O<sub>3</sub> to CeO<sub>2</sub> could modify the chemical environment around oxygen vacancies, prohibiting adsorption of Cl species. Part of the Cr<sup>3+</sup> were incorporated into the lattice of CeO<sub>2</sub>, whereas the other Cr<sub>2</sub>O<sub>3</sub> were interacted with CeO<sub>2</sub> to generate the active Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> interfaces (formation of bonds like Cr–O–Ce). In addition, formation of Cr<sup>6+</sup> species with a strong oxidizing ability was beneficial for deep oxidation of CVOCs. Furthermore, Brönsted acid sites and strong Lewis acid sites were enhanced by interaction of Cr<sub>2</sub>O<sub>3</sub> with CeO<sub>2</sub>. Since pure Cr<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> were inactive for TCE combustion at 210 °C, it is likely that good catalytic performance of 3DOM Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> was associated with the active interfaces between Cr<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>.

For total oxidation of TCE, the final products were CO, CO<sub>2</sub>, H<sub>2</sub>O, HCl, and Cl<sub>2</sub>. The HCl selectivity (S<sub>HCl</sub>) over all of the samples are also shown in Table 3. It is observed that all of the samples showed a high HCl selectivity, particularly over the 3DOM  $5.5Cr_2O_3$ –CeO<sub>2</sub> sample. Since HCl is easier to be treated and less toxic than Cl<sub>2</sub>, a high HCl selectivity would be favorable for the oxidation of TCE. Moreover, all of the samples exhibited a more than 99 % CO<sub>2</sub> selectivity. It should be pointed out that the estimated carbon and chlorine balance was 95–97 and 89–94 %, respectively. In other words, small amounts of carbon and chlorine were retained on the surface of the samples. It should be noted that there might be no formation of chromium oxychloride in the 3DOM Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> samples for TCE combustion below 340 °C since Cr<sub>2</sub>O<sub>3</sub> strongly interacted with CeO<sub>2</sub> to generate a  $Cr_2O_3$ –CeO<sub>2</sub> solid solution and partial  $Cr^{3+}$  were incorporated into the lattice of CeO<sub>2</sub>. The detailed situations need to be further investigated.

In order to examine the catalytic stability, we carried out the on-stream TCE oxidation over the 3DOM  $5.5Cr_2O_3$ –CeO<sub>2</sub> sample at 240 °C and SV = 20,000 mL/(g h), and their results are shown in Fig. 11. No significant loss in activity over 3DOM  $5.5Cr_2O_3$ –CeO<sub>2</sub> was observed after 30 h of on-stream reaction. In other words, the 3DOM  $5.5Cr_2O_3$ –CeO<sub>2</sub> sample was catalytically durable under the adopted conditions.

In order to better make a comparison on performance, Table 3 summarizes the TCE reaction rates normalized by per gram of catalyst. Obviously, the TCE reaction rate at 250 °C decreased in the order of 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> > 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> > 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> > 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> > 3DOM CeO<sub>2</sub>, with the 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> sample showing the highest TCE reaction rate ( $4.02 \times 10^{-7}$  mol/(g<sub>cat</sub> s)) at 250 °C. These

results confirm that factors, such as adsorbed oxygen species concentration, low temperature reducibility, and strong interaction between Cr<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>, could influence catalytic activity of the sample. There have been a number of works on the oxidation of TCE over various catalysts in the literature [13,45,57,61–66]. According to the results reported in the literature, one can see that the TCE reaction rate at 250 °C ( $4.02 \times 10^{-7}$ mol/( $g_{cat}$  s)) over our 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> sample was much higher than that (1.12 ×  $10^{-7} \text{ mol/(g_{cat} s))}$  over CeMn-HT-N6A4 [13], that  $(1.13 \times 10^{-7} \text{ mol/(g_{cat} s))}$  over 1.02 wt% Ru/TiO<sub>2</sub> (P25) [61], that  $(2.67 \times 10^{-8} \text{ mol/(g_{cat} s)})$  over Ce<sub>0.15</sub>Zr<sub>0.85</sub>O<sub>2</sub> [62], that  $(4.08 \times 10^{-8} \text{ mol/(g_{cat} s)})$  $mol/(g_{cat} s))$  over LaMn<sub>1.2</sub>O<sub>3</sub> [57], that  $(4.31 \times 10^{-8} mol/(g_{cat} s))$  over 4Ce1Cr-(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> [45], that  $(9.76 \times 10^{-8} \text{ mol/(g_{cat} s)})$  over 3.5 wt% VO<sub>x</sub>/TiO<sub>2</sub>-SG [63], that  $(2.67 \times 10^{-9} \text{ mol/(g_{cat} s)})$  $mol/(g_{cat} s))$  over 4.3 wt% Mn/H-ZSM-5 [64], that  $(3.49 \times 10^{-9} mol/(g_{cat} s))$  over 0.42 wt% Pd/Al<sub>2</sub>O<sub>3</sub> [65], and that  $(7.05 \times 10^{-9} \text{ mol/(g_{cat} s)})$  over CoFeAlO<sub>x</sub> [66]. Therefore, our 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> sample performed much better than most of the reported catalysts for TCE oxidation. The 3DOM structure with a larger surface area was beneficial for enhancement in adsorption and mass transfer of the reactant molecules, and the nanosized skeleton surface was favorable for improvement in reducibility. Partial Cr<sup>3+</sup> were incorporated into the lattice of CeO<sub>2</sub>, resulting in an increase in oxygen vacancy density and hence a rise in  $O_{ads}$  concentration. The interaction between  $Cr_2O_3$  and  $CeO_2$  could generate a Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> solid solution, forming the active Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> interfaces. Furthermore, the doping of chromia increased the amount of strong acid sites. Therefore, the O<sub>ads</sub> species concentration, low-temperature reducibility, and strong interaction between

 $Cr_2O_3$  and  $CeO_2$ , and strong acidity were the factors influencing the catalytic performance of 3DOM 5.5 $Cr_2O_3$ –CeO<sub>2</sub> for TCE combustion.

#### 3.5. Effects of water vapor and carbon dioxide on activity

Due to the co-existence of TCE and H<sub>2</sub>O or CO<sub>2</sub> in industrial waste gases, we examined the effects of water vapor and carbon dioxide on activity of the 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> sample at 270 °C and SV = 20,000 mL/(g h), and their results are shown in Fig. 12A and B, respectively. It was reported that activity of a catalyst was negatively influenced by water vapor introduction [27,67]. Therefore, it is highly desired to develop a water-resistant catalyst for practical applications. In the presence of 3.0 vol% water vapor, TCE conversion decreased by ca. 6 % after 6 h of on-stream reaction; a further rise in water vapor concentration to 5.0 vol% led to a drop in TCE conversion by ca. 10 %. After water vapor was cut off, TCE conversions were restored to their original values in the absence of water vapor (Fig. 12A). This result means that partial deactivation induced by water vapor addition was reversible. The inhibition of water was due to the competitive adsorption of water and reactant molecules on the active sites in the 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> sample. Similar phenomena were also observed by other researchers [26,67]. Fig. 12B shows the effect of CO<sub>2</sub> addition on catalytic activity of 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> at 270 °C and SV = 20,000 mL/(g h). Introduction of 5.0 and 10.0 vol% CO<sub>2</sub> to the reaction system led to ca. 4 and 6 % loss in TCE conversion. The negative effect of CO<sub>2</sub> addition was due to the fact that partial active sites in 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> were covered by adsorption of carbonate species formed during the on-stream reaction. After the used sample was activated in an O<sub>2</sub> flow of 20 mL/min at 400 °C for 1 h, TCE conversion slightly increased. This result

suggests that the formed carbonate species were not totally decomposed and part of the active sites occupied by carbonate species were not recovered. Therefore, partial deactivation due to  $CO_2$  addition was irreversible. Similar phenomena were also observed in our previous investigations [68,69].

#### 4. Conclusions

The 3DOM CeO<sub>2</sub>, 3DOM Cr<sub>2</sub>O<sub>3</sub>, 3DOM xCr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> samples with a surface area of 35-47 m<sup>2</sup>/g were prepared using the PMMA-templating and incipient wetness impregnation methods, respectively. The ceria in 3DOM CeO<sub>2</sub>, 3DOM xCr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> was of cubic fluorite-type crystal structure, whereas chromia in 3DOM Cr<sub>2</sub>O<sub>3</sub>, 3DOM xCr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, and 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> was of rhombohedral crystal structure. All of the samples displayed a good-quality 3DOM architecture. It is found that an appropriate amount of Cr<sub>2</sub>O<sub>3</sub> doped to CeO<sub>2</sub> could enhance the  $O_{ads}$  species concentration and low-temperature reducibility of the 3DOM  $xCr_2O_3$ –CeO<sub>2</sub> sample. The 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> sample showed the highest catalytic activity for TCE oxidation ( $T_{10\%} = 153 \text{ °C}$ ,  $T_{50\%} = 214 \text{ °C}$ , and  $T_{90\%} = 255 \text{ °C}$  at SV = 20,000 mL/(g h)) and good catalytic stability. Partial deactivation induced by water vapor addition was reversible, whereas CO<sub>2</sub> addition resulted in irreversible deactivation of 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>. It is concluded that the good catalytic performance of 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> was associated with its O<sub>ads</sub> species concentration, low-temperature reducibility, and strong interaction between Cr<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>. We believe that such 3DOM-structured chromia-ceria materials are promising catalysts for the oxidative removal of CVOCs.

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#### **Captions of Figures and Tables**

**Fig. 1.** XRD patterns of (a) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (b) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (c) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (d) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub>, (e) 3DOM CeO<sub>2</sub>, and (f) 3DOM Cr<sub>2</sub>O<sub>3</sub>.

**Fig. 2.** Raman spectra of (a) 3DOM Cr<sub>2</sub>O<sub>3</sub>, (b) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (c) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (d) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (e) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub>, and (f) 3DOM CeO<sub>2</sub>.

**Fig. 3.** SEM images of (a) 3DOM CeO<sub>2</sub>, (b) 3DOM Cr<sub>2</sub>O<sub>3</sub>, (c, d) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (e, f) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (g, h) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, and (f) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub>.

**Fig. 4.** TEM images of (a) 3DOM CeO<sub>2</sub>, (b) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, (c) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, (d) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, (e) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub>, and (f) 3DOM Cr<sub>2</sub>O<sub>3</sub>.

**Fig. 5.** HAADF–STEM and elemental mapping images of the 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> sample.

Fig. 6. (A) N<sub>2</sub> adsorption–desorption isotherms and (B) pore-size distributions of (a) 3DOM  $3.5Cr_2O_3$ –CeO<sub>2</sub>, (b) 3DOM  $5.5Cr_2O_3$ –CeO<sub>2</sub>, (c) 3DOM  $8.0Cr_2O_3$ –CeO<sub>2</sub>, (d)  $5.5Cr_2O_3/3DOM$  CeO<sub>2</sub>, (e) 3DOM CeO<sub>2</sub>, and (f) 3DOM Cr<sub>2</sub>O<sub>3</sub>.

**Fig. 7.** (A) Ce 3d, (B) O 1s, and (C) Cr 2p<sub>3/2</sub> XPS spectra of (a) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (b) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (c) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (d) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub>, (e) 3DOM CeO<sub>2</sub>, and (f) 3DOM Cr<sub>2</sub>O<sub>3</sub>.

**Fig. 8.** (A) H<sub>2</sub>-TPR profiles and (B) initial H<sub>2</sub> consumption rate versus inverse temperature of (a) 3DOM CeO<sub>2</sub>, (b) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (c) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (d) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (e) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub>, and (f) 3DOM Cr<sub>2</sub>O<sub>3</sub>.

**Fig. 9.** (A) TCE conversion as a function of temperature and (B) ln *k* versus inverse temperature over ( $\bigcirc$ ) 3DOM CeO<sub>2</sub>, ( $\bigcirc$ ) 3DOM Cr<sub>2</sub>O<sub>3</sub>, ( $\blacktriangle$ ) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, ( $\bigtriangleup$ ) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, ( $\blacksquare$ ) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, and ( $\Box$ ) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> at SV = 20,000 mL/(g h).

Fig. 10. Concentrations of the C<sub>2</sub>Cl<sub>4</sub> by-product formed over ( $\bigcirc$ ) 3DOM CeO<sub>2</sub>, ( $\bigcirc$ ) 3DOM Cr<sub>2</sub>O<sub>3</sub>, ( $\blacktriangle$ ) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, ( $\bigtriangleup$ ) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, ( $\blacksquare$ ) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, and ( $\Box$ ) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> at SV = 20,000 mL/(g h).

Fig. 11. TCE conversion as a function of on-stream reaction time over 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> at 240 °C and SV = 20,000 mL/(g h).

Fig. 12. Effects of (A) water vapor and (B) carbon dioxide on catalytic activity of 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> at 270 °C and SV = 20,000 mL/(g h).

 Table 1. BET surface areas, pore volumes, macro- and mesopore diameters of the as-prepared samples.

Table 2. Surface element compositions and H<sub>2</sub> consumption of the samples.

**Table 3.** Catalytic activities, HCl selectivity ( $S_{HCl}$ ), reaction rates at 250 °C, and apparent activation energies ( $E_a$ ) at SV = 20,000 mL/(g h) of the samples.



Fig. 1. XRD patterns of (a) 3DOM  $3.5Cr_2O_3$ -CeO<sub>2</sub>, (b) 3DOM  $5.5Cr_2O_3$ -CeO<sub>2</sub>, (c) 3DOM  $8.0Cr_2O_3$ -CeO<sub>2</sub>, (d)  $5.5Cr_2O_3/3DOM$  CeO<sub>2</sub>, (e) 3DOM CeO<sub>2</sub>, and (f) 3DOM Cr<sub>2</sub>O<sub>3</sub>.



**Fig. 2.** Raman spectra of (a) 3DOM Cr<sub>2</sub>O<sub>3</sub>, (b) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (c) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (d) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (e) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub>, and (f) 3DOM

CeO<sub>2</sub>.



**Fig. 3.** SEM images of (a) 3DOM CeO<sub>2</sub>, (b) 3DOM Cr<sub>2</sub>O<sub>3</sub>, (c, d) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (e, f) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (g, h) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, and (f) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub>.



Fig. 4. TEM images of (a) 3DOM CeO<sub>2</sub>, (b) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, (c) 3DOM

5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, (d) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, (e) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub>, and (f) 3DOM

 $Cr_2O_3$ .



Fig. 5. HAADF–STEM and elemental mapping images of the 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>

sample.



**Fig. 6.** (A) N<sub>2</sub> adsorption–desorption isotherms and (B) pore-size distributions of (a) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (b) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (c) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (d) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub>, (e) 3DOM CeO<sub>2</sub>, and (f) 3DOM Cr<sub>2</sub>O<sub>3</sub>.



**Fig. 7.** (A) Ce 3d, (B) O 1s, and (C) Cr 2p<sub>3/2</sub> XPS spectra of (a) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (b) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (c) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, (d) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub>, (e) 3DOM CeO<sub>2</sub>, and (f) 3DOM Cr<sub>2</sub>O<sub>3</sub>.



Fig. 8. (A) H<sub>2</sub>-TPR profiles and (B) initial H<sub>2</sub> consumption rate versus inverse temperature of (a) 3DOM CeO<sub>2</sub>, (b) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, (c)

3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, (d) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, (e) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub>, and (f) 3DOM Cr<sub>2</sub>O<sub>3</sub>.



**Fig. 9.** (A) TCE conversion as a function of temperature and (B) ln *k* versus inverse temperature over ( $\bigcirc$ ) 3DOM CeO<sub>2</sub>, ( $\bigcirc$ ) 3DOM Cr<sub>2</sub>O<sub>3</sub>, ( $\blacktriangle$ ) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, ( $\bigtriangleup$ ) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, ( $\blacksquare$ ) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, and ( $\Box$ ) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> at SV = 20,000 mL/(g h).



Fig. 10. Concentrations of the C<sub>2</sub>Cl<sub>4</sub> by-product formed over ( $\bigcirc$ ) 3DOM CeO<sub>2</sub>, ( $\bigcirc$ ) 3DOM Cr<sub>2</sub>O<sub>3</sub>, ( $\blacktriangle$ ) 3DOM 3.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, ( $\bigtriangleup$ ) 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, ( $\blacksquare$ ) 3DOM 8.0Cr<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>, and ( $\Box$ ) 5.5Cr<sub>2</sub>O<sub>3</sub>/3DOM CeO<sub>2</sub> at SV = 20,000 mL/(g h).



Fig. 11. TCE conversion as a function of on-stream reaction time over 3DOM  $5.5Cr_2O_3$ -CeO<sub>2</sub> at 240 °C and SV = 20,000 mL/(g h).



Fig. 12. Effects of (A) water vapor and (B) carbon dioxide on catalytic activity of 3DOM 5.5Cr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> at 270 °C and SV = 20,000 mL/(g h).

**Table 1.** BET surface areas, pore volumes, macro- and mesopore diameters of the as-prepared samples.

Sample	BET surface	Pore	Macropore	Mesopore
	area	volume	diameter <sup>a</sup>	diameter <sup>b</sup>
	$(m^2/g)$	$(cm^3/g)$	(nm)	(nm)
3DOM CeO <sub>2</sub>	47.3	0.221	140–160	3.0–4.3
3DOM 3.5Cr <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub>	43.6	0.227	145–160	2.7–4.1
3DOM 5.5Cr <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub>	42.8	0.233	140–155	2.9–4.5
3DOM 8.0Cr <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub>	40.3	0.220	140–160	3.0-4.4
5.5Cr <sub>2</sub> O <sub>3</sub> /3DOM CeO <sub>2</sub>	27.6	0.231	145–155	2.8–4.2
3DOM Cr <sub>2</sub> O <sub>3</sub>	34.9	0.210	120–140	3.1–4.3

<sup>a</sup> Data were estimated according to the SEM images;

<sup>b</sup> Data were determined by the BET method.

Sample	Surface element	H <sub>2</sub>				
	Ce <sup>3+</sup> /Ce <sup>4+</sup> Cr <sup>6+</sup> /Cr <sup>3+</sup>		$Ce^{3+}/Ce^{4+}$ $Cr^{6+}/Cr^{3+}$ $O_{ads}/O_{latt}$		Oads/Olatt	consumption <sup>b</sup>
	molar ratio	molar ratio	molar ratio	(mmol/g)		
3DOM CeO <sub>2</sub>	0.17	-	0.38	5.73		
3DOM $3.5Cr_2O_3-CeO_2$ 3DOM $5.5Cr_2O_3-CeO_2$ 3DOM $8.0Cr_2O_3-CeO_2$ $5.5Cr_2O_3/3DOM$ $CeO_2$ 3DOM $Cr_2O_3$	0.21	0.26	0.41	7.60		
	0.27	0.35	0.51	9.41		
	0.25	0.31	0.45	8.73		
	0.20	0.24	0.40	6.15		
	-	0.22	0.39	6.56		

Table 2. Surface element compositions and H<sub>2</sub> consumption of the samples.

<sup>a</sup> Data were estimated by quantitatively analyzing the XPS spectra of the samples;

<sup>b</sup> Data were obtained by quantitatively analyzing the H<sub>2</sub>-TPR profiles.

Sample	Catalytic activity		$S_{\rm HCl}{}^{\rm a}$	Reaction rate at 250	Ea	
					°C	
	$T_{10\%}$	$T_{50\%}$	$T_{90\%}$		$(\times 10^{-7} \text{ mol}/(g_{cat} s))$	(kJ/mol)
	(°C)	(°C)	(°C)			
3DOM CeO <sub>2</sub>	230	_	_	36.5	1.05	109
3DOM	180	252	300	89.4	2.13	93
3.5Cr <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub> 3DOM 5.5Cr <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub>	153	214	255	96.3	4.02	81
3DOM	170	244	288	92.1	2.47	84
8.0Cr <sub>2</sub> O <sub>3</sub> –CeO <sub>2</sub> 5.5Cr <sub>2</sub> O <sub>3</sub> /3DOM CeO <sub>2</sub>	205	283	342	89.6	2.06	90
3DOM Cr <sub>2</sub> O <sub>3</sub>	185	271	322	88.7	-	94

**Table 3.** Catalytic activities, HCl selectivity ( $S_{\text{HCl}}$ ), reaction rates at 250 °C, and apparent activation energies ( $E_a$ ) at SV = 20,000 mL/(g h) of the samples.

<sup>a</sup> HCl selectivity (S<sub>HCl</sub> (%) = [HCl]/([HCl] + 2[Cl<sub>2</sub>])) was measured at 330 °C.