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Elimination of 1,2-dichloroethane over $(Ce,Cr)_xO_2/MO_y$ catalysts (M = Ti, V, Nb, Mo, W and La)

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ABSTRACT

$(Ce,Cr)_xO_2/MO_y$ (M = Ti, V, Nb, Mo, W, La, respectively) mixed oxides are synthesized by deposition-precipitation method, and evaluated for total oxidation of gaseous 1,2-dichloroethane, a typical chlorinated organic pollutant. The characterization results show that there exists strong metal-support interaction or synergistic effect between $(Ce,Cr)_xO_2$ and MO_y. The catalytic performances of these catalysts can be related to the nature of each MO_y support, the crystal structure and composition, the surface elements distribution and the diverse redox properties of $(Ce,Cr)_xO_2/MO_y$. The improved redox property, as well as the increased content of Ce^{3+} and Cr^{6+} species on the surface can enhance the catalytic performances of the catalysts. Especially, $(Ce,Cr)_xO_2/Nb_2O_5$ exhibits the best catalytic performance. $(Ce,Cr)_xO_2/Nb_2O_5$ also represents high durability for 1,2-dichloroethane oxidation during the long-term continuous test. Moreover, though the presence of water or benzene in the reaction system slightly suppresses 1,2-dichloroethane oxidation, the catalytic activity can be recovered by the cut of water, while a little deactivation is found if benzene is removed away, since coke has been deposited on the catalyst surface by the combustion of benzene.

1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs) contain a significant class of synthetic intermediates and organic solvents widely used in industrial operations, and are usually discharged into the environment with low concentration and large volume [1–3]. These chlorinated compounds are always toxic to human beings, and they also tend to be accumulated in the atmosphere [1,4]. Catalytic oxidation (or deep oxidation) is one of the most widely adopted methods to eliminate various kinds of Cl-VOCs with low concentration (100–10,000 ppmv), mainly due to its larger treatment capacity and lower reaction temperatures (less than 500 °C) to avoid the formation of NO_x and polychlorinated byproducts [4–6].

The main catalysts studied for Cl-VOCs elimination are supported noble metal materials, zeolites and modified zeolites, perovskites and metal oxides. Previous literatures have shown that supported noble metal catalysts generally exhibits higher catalytic activities than others, but they are more expensive and easily deactivated because of Cl poisoning and the formation of metal oxychloride, resulting in the volatilization of active species and the formation of polychlorinated byproducts [4,7,8]. Though H-type zeolites and modified zeolites display noticeable catalytic activities [3,8–11], large amount of chlorinated byproducts and CO are detected in the oxidation process, and obvious deactivation caused by coke formation is also observed because of their strong acidity and poor oxidizing ability. Perovskite catalysts with high structure stability are also widely explored, but they are less active and always need higher reaction temperatures [12]. Therefore, metal oxide catalysts (such as V_2O_5, Cr_2O_3 and MnO_2 [4]) especially CeO_2 based mixed oxides (such as CeO_2-MnO_x [13], CeO_2-ZrO_2 [14] and $Ce_xPr_{1-x}O_2$ [15]) have also been extensively investigated, and in fact they exhibit considerable oxidative activities and suitable chemical resistance to Cl-poisoning. Among them, $(Ce,Cr)_xO_2$ mixed oxide with higher oxidizing ability and structure stability shows preferable catalytic performances for total oxidation of Cl-VOCs with different molecule structures [16–19], and the atom ratio of Ce/Cr in the range of 4:1 to 2:1 is the best [19]. However, to further improve the catalytic performance, both the acid and oxidative properties need to be improved, since acid center is needed to firstly break the C—Cl bond with lower bonding energy, and the oxidative center is required next for the destruction of C—C, C—H or C=O bond. Besides, it is also necessary to introduce third component as promoter to increase the selectivity to HCl rather than Cl_2, in

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order to reduce the toxicity of the final products, the deposition of Cl species and the formation of chlorinated byproducts on the surface of the catalysts. Previous literature has revealed that the addition of H-type zeolites can increase the acid property of $(Ce,Cr)_xO_2$ and thus significantly improve the catalytic activity and HCl selectivity [20], but obvious deactivation is detected due to coke formation, since there is still lack of enough oxidative sites. Therefore, the introduction of high-valence metal ions with the combination of acid and oxidative properties is promising.

The scope of this work is to systematically investigate the structure-activity relationship for 1,2-dichloroethane (DCE) oxidation over a series of $(Ce,Cr)_xO_2/MO_y$ mixed oxides (M = Ti, V, Nb, Mo, W and La, respectively). It concentrations on investigating the effect of the inherent nature of each metal oxide support, the strong metal-support interaction (SMSI) as well as the acid and redox properties of the materials on the catalytic activity, selectivity and durability for the elimination of DCE, a typical chlorinated organic pollutant. Moreover, the influence of water vapor or non-chlorinated VOCs in the reaction system on the destructive efficiency of the catalysts, is further explored, in order to simulate the real conditions for industrial application.

2. Experimental method

2.1. Catalyst preparation

The supports MO_y (M = Ti, V, Nb, Mo, W and La, respectively) were purchased from Guoyao company and further calcined in air (500 °C, 2 h), followed by mechanical milling for 0.5 h.

$(Ce,Cr)_xO_2/MO_y$ (mass ratio of $(Ce,Cr)_xO_2$ to MO_y was 1:1) were prepared by traditional deposition-precipitation method. Firstly, a certain amount of MO_y was added into the mixed solution of quantified $Ce(NO_3)_3$ and $Cr(NO_3)_3$ (atom molar ratio of Ce/Cr was 4:1), and then ultrasonic concussion for 1 h. Afterwards, 0.50 mol L^{-1} $(NH_4)_2CO_3$ was added dropwise into the above solution under vigorous stirring, and the final pH of the solution reached 9.0. Upon aged at 25 °C for 12 h, the precipitated solids were filtered, washed by distilled water and then dried in ethanol under super critical condition (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 $(Ce,Cr)_xO_2/MO_y$, and the content of Ce and Cr was 36.6%wt and 3.4%wt, respectively. For comparison, CeO_2/Nb_2O_5 and CrO_x/Nb_2O_5 were synthesized, and the content for Ce or Cr is 40.0%wt. $(Ce,Cr)_xO_2$ mixed oxide was also prepared following a similar procedure, and the contents of Ce and Cr are double than those for $(Ce,Cr)_xO_2/MO_y$.

All the samples were finally pressed into pellets and sieved to 40–60 mesh (0.3–0.45 mm) before used.

2.2. Catalyst characterization

The X-ray diffraction (XRD), UV-Raman spectroscopy, N_2 adsorption-desorption, scanning electron microscopy (SEM) and H_2 temperature-programmed reduction (H_2-TPR) characterizations were described in previous reference [18]. NH_3 temperature-programmed desorption (NH_3-TPD) experiment was given in [20] and 0.2 g sample was used each time in this work. The X-ray photoelectron spectroscopy (XPS) patterns of the materials were collected on the Thermo K-Alpha using Al-Kα radiation at 1486.6 eV/12.5 Kv, and all the spectra were calibrated based on the binding energy of C_{1s} (284.6 eV). The deconvolution of the peaks in XPS profiles was carried out using the CasaXPS software, in which the curve fitting was performed using the Gaussian–Lorentzian peak shape and Shirley type background subtraction.

2.3. Evaluation of catalytic performances

The catalytic performances of the catalysts were measured in a traditional quartz fixed-bed reactor (6 mm i.d.), and 500 mg catalyst (0.3–0.45 mm) was used each time. The reaction feed consisted of ~1000 ppmv DCE using dry air as the balance gas, and GHSV = 9, 000 mL $g_{cat}{}^{-1}$ h^{-1} with a total flow of 75 mL min^{-1}. The concentration of the reactant, the byproducts and the final products CO_x in the outlet of the gas flow was analyzed on-line at given temperatures by GC equipped with TCD and FID detectors. Selectivity to HCl and Cl_2 was also measured by the method mentioned in previous reference [16]. In order to further investigate the mixture effect, additional ~1000 ppmv benzene or 2.3% water vapor was injected into the reaction system. The durability of the catalysts for total oxidation of DCE was evaluated under the same condition.

3. Results and discussion

3.1. Results of catalytic performance evaluation

3.1.1. Catalytic performances for DCE destruction

Previous experiments have shown that mass transfer limitation is absent under this test condition, and no obvious DCE conversion is observed below 420 °C in blank test. Fig. 1(A) and (B) demonstrate the catalytic activities of pure $(Ce,Cr)_xO_2$, pure MO_y and $(Ce,Cr)_xO_2/MO_y$ catalysts for total oxidation of DCE. As shown in Fig. 1(A), pure MO_y and $(Ce,Cr)_xO_2$ represent diverse catalytic activities. Based on the values of $T_{50\%}$ (temperature at which the conversion of the reactant reaches 50%), the apparent catalytic activity decreases in the order of $(Ce,Cr)_xO_2$ (225 °C) $\succ$ TiO_2 (243 °C) $\succ$ La_2O_3 (296 °C) $\succ$ Nb_2O_5 (304 °C) $\succ\succ$ V_2O_5 (438 °C) $\succ$ WO_3 $\succ$ MoO_3, which can be related to the inherent nature of each metal oxide. Interestingly, for the $(Ce,Cr)_xO_2/MO_y$ catalysts, the apparent catalytic activities are improved at different levels based on the values of $T_{50\%}$, in the order of $(Ce,Cr)_xO_2/Nb_2O_5$ (237 °C) $\succ$ $(Ce,Cr)_xO_2/TiO_2$ (245 °C) $\succ$ $(Ce,Cr)_xO_2/WO_3$ (254 °C) $\succ$ $(Ce,Cr)_xO_2/MoO_3$ (264 °C) $\succ$ $(Ce,Cr)_xO_2/La_2O_3$ (268 °C) $\succ\succ$ $(Ce,Cr)_xO_2/V_2O_5$ (418 °C), implying that there exists synergistic effect between $(Ce,Cr)_xO_2$ and MO_y. For comparison, the catalytic activities of CeO_2/Nb_2O_5 and CrO_x/Nb_2O_5 are also evaluated, and the details are shown in Fig. SM1 in the Supplementary Material. As shown in Fig. SM1, $(Ce,Cr)_xO_2/Nb_2O_5$ represents higher activity than CeO_2/Nb_2O_5 or CrO_x/Nb_2O_5, indicating that there also exists synergy between CeO_2 and CrO_x, which is beneficial for DCE oxidation. Moreover, the TOF values for DCE oxidation over these catalysts are also calculated, since the values for the specific surface area of these catalysts are different (shown in Table 1) and obvious thermal effect may exist at higher DCE conversion. As listed in Table 1, the TOF values decrease in the order of $(Ce,Cr)_xO_2/Nb_2O_5$ $\succ$ $(Ce,Cr)_xO_2/WO_3$ $\succ$ $(Ce,Cr)_xO_2/TiO_2$ $\succ$ $(Ce,Cr)_xO_2/V_2O_5$ $\succ$ $(Ce,Cr)_xO_2$ $\succ$ $(Ce,Cr)_xO_2/La_2O_3$ $\succ$ $(Ce,Cr)_xO_2/MoO_3$, indicating that $(Ce,Cr)_xO_2/Nb_2O_5$ represents the highest inherent catalytic activity. Besides, the values of apparent activation energy (Ea) for these catalysts are also calculated, assuming DCE concentration having no obvious change within 20% conversion. As listed in Table 1, Ea values for $(Ce,Cr)_xO_2/MO_y$ are in the range of 35–47 kJ/mol, similar to or even smaller than that of $(Ce,Cr)_xO_2$. It is notable that these values are much smaller than those for the related support MO_y, further implying that there exists synergistic effect between $(Ce,Cr)_xO_2$ and MO_y.

For catalytic elimination of Cl-VOCs, any possible byproducts should be detected carefully, since they may be more toxic and more difficult to be destroyed. As shown in Fig. 1(C) and (D), within the detection limit of TCD and FID detector, C_2H_3Cl is the sole byproduct detected during DCE oxidation,