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Synergistic performance between oxidizability and acidity/texture properties for 1,2-dichloroethane oxidation over $(Ce,Cr)_xO_2$/zeolite catalysts

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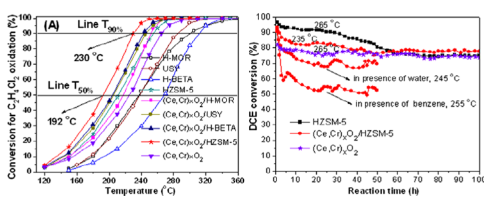
HIGHLIGHTS

- $(Ce,Cr)_xO_2$/zeolite catalysts with abundant oxidative and acid sites are prepared.
- Synergy between $(Ce,Cr)_xO_2$ and zeolite evidently promotes deep oxidation of $C_2H_4Cl_2$.
- $(Ce,Cr)_xO_2$/HZSM-5 with equivalent mass of $(Ce,Cr)_xO_2$ and HZSM-5 is the best.
- Presence of water obviously reduces accumulation of Cl species and coke formation.
- Partial deactivation at lower temperature is due to coke, H_2O and Cl adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

$(Ce,Cr)_xO_2$/zeolite catalysts with Ce/Cr molar ratio of 4:1 and equivalent mass of $(Ce,Cr)_xO_2$ and zeolite are prepared by a deposition–precipitation method, and tested for deep catalytic oxidation of 1,2-dichloroethane. Based on the values of $T_{90\%}$ (temperature at which 90% conversion is obtained), the catalytic activity decreases in the order of $(Ce,Cr)_xO_2$/HZSM-5 (230 °C) > $(Ce,Cr)_xO_2$/H-BETA (243 °C) > $(Ce,Cr)_xO_2$/USY (247 °C) > $(Ce,Cr)_xO_2$/H-MOR (253 °C), which is improved obviously than $(Ce,Cr)_xO_2$ and parent zeolites, indicting the existence of synergistic effect between $(Ce,Cr)_xO_2$ and zeolites. This synergy is resulted from that the strong acid sites of the zeolites firstly promotes 1,2-dichloroethane adsorption and dehydrochlorination, while the strong oxidative sites of $(Ce,Cr)_xO_2$ is in favor of the deep oxidation of the reactants, the intermediates and byproducts as well as the reduction of coke and Cl accumulation on the catalyst surface. Especially, $(Ce,Cr)_xO_2$/HZSM-5 represents the best catalytic activity and durability, which is also related to its special intersectional pore structure. Moreover, though the presence of benzene or water decreases the catalytic activity in the initial stage because of the competitive adsorption on active sites, $(Ce,Cr)_xO_2$/HZSM-5 represents good durability during the prolonged reaction time.

1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs), such as 1,2-dichloroethane (DCE), are widely used and emitted into the atmosphere from lots of industrial operations (Huang et al., 2014; Den et al., 2006; Ojala et al., 2011). These compounds are well known

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for their high volatility, toxicity and stability. Deep catalytic oxidation is an effective technology for the elimination of dilute concentration Cl-VOCs with complex components and high flow rate, because of its higher efficiency and lower operating temperature (Erlt et al., 2008; Aranzabal et al., 2006; Balzhinimaev et al., 2010; Paukshtis et al., 2010). For deep catalytic oxidation of various Cl-VOCs, breaking the C–C, C–H, C–O and C–Cl bond is necessary. Acid sites are firstly required to cut the C–Cl bond with lower bonding energy, and then the oxidative sites are demanded to completely destroy the intermediates and byproducts (Erlt et al., 2008; Yang et al., 2013).

In recent years, zeolite-based catalysts have been widely investigated, because of their special pore structure, shape-selective catalyzing ability, proper strong/weak acid properties and good thermal stability. Previous literatures have reported that H-type zeolites exhibit high catalytic activity for Cl-VOCs destruction and high selectivity to HCl formation (González-Velasco et al., 2000; López-Fonseca et al., 2000a; Intriago et al., 2006). However, notable CO and byproducts as well as obvious deactivation by coking are also observed at the same time, because of the poor oxidizing ability of the zeolites. Although the impregnation of transition metal oxides or noble metals is always considered, the synergy between oxides/noble metals and zeolites can hardly reach the best, and thus, the similar problems still exist (Guisnet et al., 2009; Aranzabal et al., 2009; López-Fonseca et al., 2005; Gutiérrez-Ortiz et al., 2003; Chatterjee et al., 1992). CeO_2-based catalysts, especially CeO_2-transition metal mixed oxides, have also attracted considerable interest (Harmsen et al., 2001; Wang et al., 2009; de Rivas et al., 2011, 2012; Yang et al., 2015a, 2014, 2015b), since CeO_2 can undergo a rapid and reversible redox cycle of $Ce^{4+} \leftarrow\rightarrow Ce^{3+}$, coupled with its strong interaction with other active metal, which is helpful to stabilize the active components and improve the redox property. Among the CeO_2-based catalysts, $(Ce,Cr)_xO_2$ mixed oxide exhibits outstanding catalytic performances for deep oxidation of Cl-VOCs with quite different molecule structures, because of its very high oxidizing ability.

Based on these previous research results mentioned above, in this paper, a series of $(Ce,Cr)_xO_2$/zeolites are synthesized by the deposition–precipitation method and their catalytic performances for deep catalytic oxidation of DCE, a typical model for the Cl-VOCs, are evaluated. The catalysts are characterized by means of XRD, N_2 adsorption–desorption, NH_3-TPD and H_2-TPR and O_2-TG-MS techniques. The scope of this paper is to obtain some insight into the effect of the synergy between $(Ce,Cr)_xO_2$ and zeolites on the activity, selectivity and durability for DCE oxidation, which may be responsible for promoting the catalytic performance. Moreover, the presence of benzene and water on the catalytic performances of the $(Ce,Cr)_xO_2$/HZSM-5 catalyst, along with the reason for the partial deactivation in the initial stage of the long-term continuous durability test, has also been explored.

2. Material and methods

2.1. Catalyst preparation

Zeolites were purchased from Nanhua Catalyst Company. The molar ratio of SiO_2/Al_2O_3 was 25 for H-MOR, H-BETA and HZSM-5, whereas 5.2 for USY, respectively.

$(Ce,Cr)_xO_2$ mixed oxide was prepared by the coprecipitation method. 0.50 mol L^{-1} $(NH_4)_2CO_3$ solution was added dropwise into 300 mL mixed solution of 0.20 mol L^{-1} $Ce(NO_3)_3$ and 0.050 mol L^{-1} $Cr(NO_3)_3$ under vigorous stirring. The final pH of the solution was 9.0. After 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, 7.5 MPa, 2 h) as well as calcined in air at 500 °C for 2 h. The obtained catalyst was named as $(Ce,Cr)_xO_2$, and the atom molar ratio of Ce/Cr was 4:1.

$(Ce,Cr)_xO_2$/zeolites (zeolite represents H-MOR, USY, H-BETA and HZSM-5, respectively) were prepared by the deposition–precipitation method. Zeolite was firstly dispersed into 300 mL mixed solution of 0.20 mol L^{-1} $Ce(NO_3)_3$ and 0.050 mol L^{-1} $Cr(NO_3)_3$, and its preparation is same to that of $(Ce,Cr)_xO_2$. The obtained catalyst was named as $(Ce,Cr)_xO_2$/H-MOR, $(Ce,Cr)_xO_2$/USY, $(Ce,Cr)_xO_2$/H-BETA and $(Ce,Cr)_xO_2$/HZSM-5, respectively, and the mass ratio of $(Ce,Cr)_xO_2$ to zeolite was 1:1. The metal loading for Ce and Cr is 36.6 wt% and 3.4 wt%, respectively.

For comparison, CeO_x, CrO_x, CeO_x/HZSM-5 (40 wt% Ce) and CrO_x/HZSM-5 (40 wt% Cr) were also prepared by the same method.

Finally, the above catalysts were pressed into pellets and sieved to 40–60 meshes (0.3–0.45 mm).

2.2. Catalyst characterization

The characterization of X–ray diffraction (XRD), N_2 adsorption–desorption, ammonia temperature-programmed desorption (NH_3-TPD) and hydrogen temperature-programmed reduction (H_2-TPR) experiments were described in detail in previous reference (Yang et al., 2013). For NH_3-TPD and H_2-TPR measurements, the catalysts were firstly pretreated in an Ar flow (99.999%, 40 mL min^{-1}) at 400 °C for 0.5 h. The heating rate is 10 °C min^{-1} in the process.

The loss of Cr content for used $(Ce,Cr)_xO_2$/HZSM-5 catalyst was analyzed by ICP-MS (IRIS Intrepid II XSP). Before measurement, fresh and used catalysts were pretreated in dry air at 400 °C for 2 h, in order to remove the adsorbed substances on the catalyst surface.

TG-MS measurement for used catalysts was performed on a Thermogravimetric Analyzer (TGA, Perkin Elmer Inc., USA) connected with a MS apparatus (HIDEN QJC-20). After pretreated in a Ar flow (99.999%, 10 mL min^{-1}) at 120 °C for 2 h, the catalysts were further heated to 800 °C at the rate of 10 °C min^{-1} in a O_2 flow (99.999%, 10 mL min^{-1}).

2.3. Evaluation of catalytic performance

The catalytic performances of the catalysts were conducted in a quartz fixed-bed reactor (6 mm i.d.). 500 mg catalyst (0.3–0.45 mm) was used. The reaction feed was ~1000 ppmv DCE with dry air as the balance gas, and GHSV was 9000 mL g^{-1} h^{-1} with a total flow of 75 mL min^{-1}. The components in the outlet were analyzed on-line using GC equipped with FID and TCD detector. At each given temperature, the catalytic performances were evaluated after being stabilized for 30 min. More information was described in the Ref. Yang et al. (2015a). Durability tests were carried out under different conditions, and the catalytic activities were measured similar to that mentioned above.

DCE adsorption and its temperature-programmed surface reaction (TPSR) over the catalysts were also performed. The catalyst was firstly pretreated in an Ar flow (99.999%, 75 mL min^{-1}) at 400 °C for 0.5 h. After being cooled down to 50 °C, 1000 ppmv DCE (20% O_2/Ar as the balance gas) was injected into the reaction system. After reaching the adsorption–desorption equilibrium, the catalyst was heated from 50 to 550 °C at the rate of 5 °C min^{-1} in the 1000 ppmv DCE (20% O_2/Ar as the balance gas) with a total flow of 75 mL min^{-1}. The concentration of DCE, the byproduct C_2H_3Cl and the products (CO, CO_2, HCl and Cl_2) was measured on-line by MS (HIDEN QJC-20).