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A two-stage $Ce/TiO_2–Cu/CeO_2$ catalyst with separated catalytic functions for deep catalytic combustion of CH_2Cl_2

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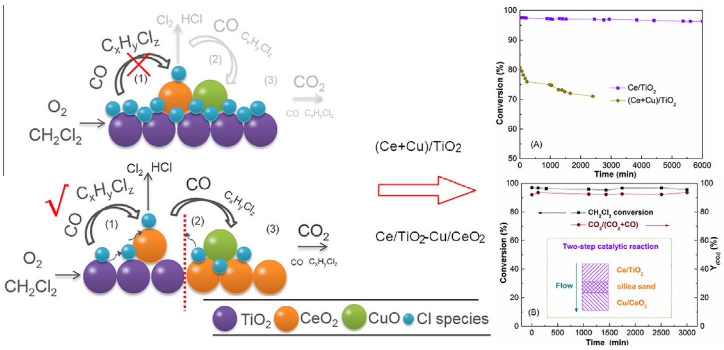
HIGHLIGHTS

- A two-stage $Ce/TiO_2–Cu/CeO_2$ catalyst was for the first time fabricated for the total oxidation of DCM.
- A three-step degradation mechanism has been proposed for the $(Ce+Cu)/TiO_2$ catalyst.
- CuO had a good resistance to Cl poisoning by itself.

GRAPHICAL ABSTRACT



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ABSTRACT

For the deep combustion of dichloromethane (DCM), a novel two-stage $Ce/TiO_2–Cu/CeO_2$ catalyst was designed and its catalytic performance was investigated in this study. It yielded a remarkable catalytic activity. The degradation efficiency reached up to 97.0% at 330 °C with less undesired CO, Cl_2 and byproducts ($C_xH_yCl_z$) in dry air. The DCM conversion and the yield of CO_2 maintained during the long time test, even in the presence of water. Based on the comparison of catalytic performance and catalyst characterization of Ce/TiO_2 and $(Ce+Cu)/TiO_2$, a three-step degradation mechanism for DCM was proposed. The mechanism consisted of adsorption and rupture of the C–Cl bonds, deep oxidation of C–H from byproducts and total oxidation of CO to CO_2, which afforded the theoretical basis for the design of the novel two-stage catalytic system. In the novel two-stage $Ce/TiO_2–Cu/CeO_2$ system, the rupture of C–Cl and the total oxidation of CO were physically isolated. This separated arrangement not only avoided the decrease of acid sites happened on $(Ce+Cu)/TiO_2$ catalyst, but also avoided the chlorine poisoning of TiO_2 due to the strong adsorption of Cl on the CuO. Moreover, CuO itself had high resistance to the toxicity of Cl.

1. Introduction

Chlorinated volatile organic compounds (CVOCs), such as CH_2Cl_2 (dichloromethane, DCM), are considered as one of the main air pollution due to their toxic nature and to their risk on the environment and human health [1–3]. The control of the release of CVOCs is just around the corner and the catalytic combustion route

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would be one of the most promising techniques, which needs suitable catalysts for its widespread industrial applications [4–6].

In the development of advanced catalysts for degradation of CVOCs, the high activity, low level of byproducts, total oxidation of CO to CO_2, selectivity to HCl and the anti-toxicity of Cl remain as the great challenges [7–9].

Noble metals based catalysts exhibited excellent activity in the oxidation of CVOCs while these kinds of catalysts suffered from the high cost and the low resistance to chlorine poisoning [10–12]. Alternatively, the transition metal oxides based catalysts have gained more and more attentions because of their high reaction activity and better stability for the catalytic combustion of CVOCs, such as Co_3O_4 [13,14], V_2O_5/TiO_2 [15], CeO_2-USY [16], Mn–Zr mixed oxides [17], Ce/Zr mixed oxides [18], SnO_x–MnO_x–TiO_2 catalysts [19].

In our previous research [20], it found that Ce/TiO_2 catalyst was a potential candidate for the deep combustion of dichloromethane (DCM) due to its abundant acid sites and good redox property. The abundant acid sites were related to TiO_2 support and were responsible for the adsorption and rupture of C–Cl bonds and partial dissociation of C–H bonds. The good redox property was ascribed to ceria and led to the dissociation of C–H bonds and the certain oxidation of CO to CO_2. Furthermore, the poison of Cl for Ce/TiO_2 was inhibited to some extent by CeO_2 due to the rapid removal of Cl on the surface of CeO_2. However, for Ce/TiO_2 catalyst, CO was still dominated in the exhaust gases and it was not a satisfied result.

Copper oxide and copper oxide doped materials have been certified as active catalystsin deep oxidation reaction, especially in the oxidation of CO [21–25]. CuMgAl mixed oxides, obtained from hydrotalcite-like compounds, presented higher catalytic activity for the catalytic combustion of trichloroethylene than that of hydrotalcite-derived mixed oxides without copper due to its important redox properties [21]. More important, the main oxidation product was CO_2 and no CO was observed at any temperature. The catalysts CuO-USY [16], $Cu_{0.13}Ce_{0.87}O_y$ [23], $Cu_{1.5}Mn_{1.5}O_4$ [24] and Au–Cu/CeO_2 [25] also showed better performance in the total oxidation of volatile organic compounds. Moreover, copper-based compounds (such as CuO [26,27], $CuCl_2$ [28]) were the basal catalysts for Deacon reaction (DR) to produce Cl_2 from HCl at above 350 °C. It meant that the resistance to Cl species of these compounds would be enhanced in such reaction temperature. Thus, it might be a good choice to introduce the copper oxide to the Ce/TiO_2 catalyst for deep catalytic combustion of CH_2Cl_2.

For the addition of copper, the traditional strategy was to add CuO into the Ce/TiO_2 directly with co-impregnation method. However, this addition method would change the chemical and physical properties of Ce/TiO_2. For Ce/TiO_2, the DCM conversion was good and the catalytic activity was stable in 100 h test [20]. The dominated CO in the exhaust was the sole problem to be solved. In this opinion, a two-stage catalyst with the separated catalytic functions could be an alternative solution for the exhausted CO. The former stage was worked for the rupture of C–Cl bonds and partial dissociation of C–H bonds, and the other stage was focused on the oxidation of CO. In this work, two strategies for the addition of copper were adopted for the modification of Ce/TiO_2 and two kinds of catalysts were prepared for the deep catalytic combustion of DCM (model of short-chain chlorinated VOCs). The degradation performance of DCM, the byproducts, the degree of total oxidation and the tolerance to chlorine of the catalysts were investigated and compared. The structure and surface chemical properties of these catalysts were characterized by using XRD, BET, XPS, NH_3-TPD, H_2-TPR and DRIFT methods. Special attention was paid to the correlation between the layout pattern of catalyst and the degradation performance. We expect that the developed two-stage catalyst arrangement and the findings present herein could give some new insights in the design and syntheses of catalysts for catalytic oxidation of CVOCs.

2. Experimental

2.1. Catalyst preparation

All reagents used in the present work were of analytical grade.

Nano-sized anatase TiO_2 was prepared by hydrothermal process [29,30]. In a typical preparation, titanium butoxide was dissolved in anhydrous ethanol (the molar ratio of butoxide:ethanol = 1:15). Then the butoxide solution was added to a water–ethanol solution (the molar ratio of water:ethanol = 5:1) and the final molar ratio of water: ethanol: butoxide was 50:25:1. A white precipitate of amorphous oxides was produced and stirred at normal temperature for 2 h. Then the mixture was transferred to a 200 ml stainless steel autoclave and kept at 180 °C for 24 h. After hydrothermal crystallization, the precipitate was collected by centrifugation and washed with deionized water five times. After dried at 80 °C and calcined at 450 °C in air for 3 h, the required TiO_2 was prepared.

Pure CeO_2 and CuO were prepared from the thermal decomposition of ceria nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) and cupric nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) at 450 °C in air for 3 h.

The introduction of ceria and copper oxide into the TiO_2 supports was conducted by impregnating the titanium support with the required amount of cerium nitrate and cupric nitrate solution. The mixture was stirred for 6 h, dried and calcined at 450 °C for 3 h to obtain the final sample for further analysis and examination. The catalysts were designated as Ce/TiO_2 (Ce/Ti molar ratio at 1:19), (Ce+Cu)/TiO_2 (Ce/Ti molar ratio at 1:19, Cu/Ti molar ratio at 0.3:19 or 0.3:1, in the paper, (Ce+Cu)/TiO_2 represented the Ce/Cu/Ti molar ratio at 1:0.3:19 if there was no special notes), Cu/TiO_2 (Cu/Ti molar ratio at 0.3:19 or 0.3:1).

The introduction of copper oxide into the CeO_2 supports was conducted by impregnating the cerium dioxide support with the required amount of cupric nitrate solution and the subsequent steps were operated as mentioned above. The catalysts was designated as Cu/CeO_2 (Cu/Ce molar ratio at 0.3:1).

The powder XRD patterns [16,26,31], surface chemical properties and structure data of the Ce/TiO_2, (Ce+Cu)/TiO_2 and Cu/CeO_2 samples were given in Fig. S1, Table S1 and Table S2.

For the two-stage catalyst system Ce/TiO_2–Cu/CeO_2, the first stage was Ce/TiO_2 and the second stage was Cu/CeO_2. The two stages of the catalysts had the same loading in the reactor. A little amount of silica sand was placed between the two beds for the separation of two catalysts. In Table. S3, it explained why Cu/CeO_2 was chosen as the second stage catalyst compared with CuO and Cu/TiO_2.

2.2. Catalyst characterization

The crystal phases of the samples were analyzed by using an X-ray diffractometer (XRD: model D/max RA, Riga ku Co., Japan; Cu Kα radiation, 0.15418 nm). The data were collected for scattering angles (2θ) ranging between 10° and 80° with a step size of 4°.

Nitrogen adsorption–desorption isotherms were obtained using a nitrogen adsorption apparatus (Beijing JWGB Sci.&Tech. Co., Ltd). All the samples were degassed at 200 °C prior to measurements. The Brunauer–Emmett–Teller specific surface area was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range from 0.05 to 0.30.

X-ray photoelectron spectroscopy with Al Kα X-ray ($h\nu$ = 1486.6 eV) radiation operated at 150 W (XPS: Thermo ESCALAB 250, USA) was used to investigate the surface properties and to probe the total density of states (DOS) distribution in the valence