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Catalytic combustion of chlorobenzene over VO_x/CeO_2 catalysts

Hao Huang, Yufeng Gu, Jian Zhao, Xingyi Wang *

Lab for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, PR China

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ABSTRACT

VO_x/CeO_2 catalysts with various loadings of VO_x were prepared by wet impregnation method and used in catalytic combustion of chlorobenzene (CB). Characterized by XRD, Raman, XPS, HRTEM, H_2-TPR, and O_2-TPD revealed that VO_x on CeO_2 support was identified as monomeric, oligomeric, or polymeric VO_x and $CeVO_4$. Monomeric VO_x promoted oxygen vacancies and hence increased in surface oxygen and oxygen mobility. VO_x/CeO_2 catalysts had considerable activity for CB combustion. The highest value of TOF (0.023 min^{-1}) was obtained on VO_x/CeO_2 catalysts with monomeric VO_x. VO_x greatly improved the stability of VO_x/CeO_2 catalysts through retarding the exchange of Cl for basic surface lattice oxygen of CeO_2. High stability maintained at 285 °C for at least 1000 min. *In situ* FTIR and Raman indicated that CB adsorption on CeO_2 was much stronger than VO_x, and different reaction pathways were related to different types of oxygen species existing on the surface of VO_x/CeO_2 catalysts.

1. Introduction

Dioxins and polychlorinated aromatic compounds (i.e., polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs)) are considered to be extremely hazardous contaminants due to their potential toxicity as carcinogens and teratogens, bioaccumulation in animals, and long-term persistence in the environment [1,2]. As a result, stringent environmental regulations have been imposed on the emissions containing such compounds in many countries [3]. Catalytic combustion has been proven to be a promising technology for the removal of dioxins in waste gases, due to its high effectiveness (between 250 and 550 °C) and low consumption of energy (without additional fuel) when compared to a thermal process [3]. Owing to the high toxicity of dioxins and safety for manipulation in laboratories, model reagents such as chlorobenzene (CB) and dichlorobenzene (DCB) are employed to predict the destruction behavior of dioxins on different catalysts [4].

Of the catalysts used in the studies of CB catalytic combustion, most have been reported on two types of catalysts based on noble metals (Pt [5–8], Pd [9], Au [10], Ru [11]) and transition metals (Cu [12], Fe [13], U [3,14], Cr [15], Ce [16], Co [17], Mn [18], V [19], oxides). Although noble metal catalysts exhibit higher activities, they suffer from high cost and low stability due to chlorine poisoning. Moreover, they also catalyze further polychlorinated compounds in the pollutants [5–10]. Thus far, more efforts have been devoted to transition metal oxide catalysts [13–19]. In particular, the V_2O_5-based catalysts supported on TiO_2 (or containing Mo or W oxides) have been employed commercially for the oxidative destruction of chlorinated aromatic compounds [19–26].

Our previous work indicated that high activity for CB catalytic combustion of CeO_2-based catalysts mainly owed to the unique redox properties and highly dissociation of C—Cl of CeO_2 [16,27,28]. However, stability of CeO_2 can only be achieved at a higher temperature because of the strong adsorption of inorganic chlorine species produced during the decomposition of CB on the active sites [16,27,28]. The modification of CeO_2-based catalysts with transition metal oxides that promote the stable activity at lower temperature is still a challenge. To our best knowledge, V_2O_5 was found to be suitable for the chemical resistance to chlorine poisoning [19–26]. It is expected that introduction of V_2O_5 could improve the ability of CeO_2 resistant to poisoning by Cl species. However, few studies on the behaviors of VO_x/CeO_2 catalysts in the oxidation of chlorinated volatile organic compounds were available. In this study, VO_x/CeO_2 catalysts with various loadings of VO_x were prepared by wet impregnation method and investigated in CB catalytic combustion by *in situ* technologies (*in situ* FTIR and Raman) and information on kinetics was concluded.

2. Experimental

2.1. Catalyst preparation

CeO_2 support was prepared by a hydrothermal method. Typically, 10 g of $Ce(NO_3)_3{\cdot}6H_2O$ was dissolved in 40 mL of

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* Corresponding author. Fax: +86 21 64253372.
E-mail address: wangxy@ecust.edu.cn (X. Wang).

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deionized water. After stirring the solution at room temperature (RT) for 0.5 h, 3 g of urea was added under vigorous stirring. The mixture was kept under stirring for 1 h after the formation of milky slurry. Then, the emulsion was transferred into a Teflon-lined stainless steel autoclave and heated at 140 °C for 5 h. After hydrothermal treatment, the precipitates were washed with distilled water and ethanol, and then dried at 110 °C for 12 h. Finally, the solids obtained were heated to 450 °C at a rate of 1 °C/min and calcined in air at 450 °C for 4 h.

VO_x/CeO_2 catalysts were prepared by wet impregnation of as-synthesized CeO_2 with the solution of NH_4VO_3 and oxalic acid (n_{NH4VO3}:$n_{oxalic\ acid}$ = 1:1). The impregnated solids were dried at 110 °C for 12 h and then calcined according to the same method as that for CeO_2. The catalysts are denoted as yV where y represents the weight percent (wt.%) of vanadium on CeO_2 (y = 0.2, 0.5, 0.9, 1.4, 2.1, 2.7, 4, 8). For example, 0.5V refers to 0.5 wt%V/CeO_2 sample.

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) patterns of samples were recorded on a Rigaku D/Max-rC powder diffractometer using Cu Kα radiation (40 kV and 100 mA). The diffractograms were recorded within the 2θ range of 10–80°, with a 2θ step of 0.01°, and a time step of 10 s. High-resolution transmission electron microscope (HRTEM) was taken with an FEI Tecnai G2-F20 S-TWIN microscope at an acceleration voltage of 200 kV. Scanning transmission electron microscope (STEM, Tecnai F20-FEI, 200 kV) equipped with energy-dispersive X-ray spectroscopy (EDS, Tecnai 136-5-EDAX) was used to explore the distribution of elements over the prepared samples. The nitrogen adsorption and desorption isotherms were measured at 77 K on a Micromeritics ASAP 2400 system operated in static measurement mode. Samples were outgassed at 350 °C for 4 h before the measurement. The specific surface area was calculated by using the BET model. The actual vanadium contents were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Varian 710 spectrometer. Samples were dissolved by using aqua regia–hydrogen peroxide system to form a homogeneous solution. The X-ray photoelectron spectroscopy (XPS) measurements were made on a VG ESCALAB MK II spectrometer by using Mg Kα (1253.6 eV) radiation as the excitation source. Charging of samples was corrected by setting the binding energy of adventitious carbon (C1s) at 284.6 eV. The powder samples were pressed into self-supporting disks, loaded into a sub-chamber, which was evacuated for 4 h prior to the measurements at 298 K. Temperature programmed reduction by hydrogen (H_2-TPR) was carried out in a conventional apparatus equipped with TCD. The samples (100 mg) were first pre-treated at 450 °C with 5% O_2/Ar flow (30 mL/min) for 2 h before cooled to room temperature. Then, the test was performed by heating the samples in 5% H_2/Ar flow (30 mL/min) at a heating rate of 10 °C/min from 50 °C to 750 °C. The extent of reduction was quantitatively calculated according to the TPR peak areas, and the result was calibrated on the basis of the hydrogen consumption from the reduction of CuO to Cu. Temperature programmed desorption by oxygen (O_2-TPD) was carried out in a U-shaped quartz tube and the desorption signal of oxygen was recorded with an online mass spectrometer apparatus (MS) (HIDEN, QIC-20). Prior to each test, the sample (100 mg) was pre-treated in a purified oxygen stream at 450 °C for 60 min, cooled down to room temperature in oxygen atmosphere, and purged by a stream of purified He until stabilization of MS baseline. The reactor was heated at the rate of 10 °C/min from 50 to 800 °C. Simultaneously, the desorbed oxygen signal was collected by MS detector. Temperature programmed surface reaction (TPSR) measurement was carried out under the condition same as in catalytic activity tests. First, feed containing 1,000 ppm CB, 10% oxygen, and Ar balance flowed continuously over the samples at 100 °C. After the adsorption–desorption reached an equilibrium, the samples were heated from 100 °C to a specified temperature at the heating rate of 10 °C/min. The reactant and the products (such as CB (m/z = 112), CO_2 (44), CO (28), Cl_2 (70), HCl (36), DCB (146), and B (78)) were analyzed online over a mass spectrometer apparatus (HIDEN, QIC-20).

2.3. Catalytic activity measurements

Catalytic combustion reactions were carried out at atmospheric pressure in a continuous flow micro-reactor of a quartz tube of 4 mm inner diameter. 200 mg catalyst (grain size, 40–60 mesh) was packed in the reactor bed. Before testing the activity and selectivity of VO_x/CeO_2 catalysts, the transport effects were investigated to ensure that experimental results were not significantly influenced by interphase transportation. Calculation of the theoretical external transfer rate of reactants to the catalytic particles (at a typical temperature 300 °C) based on estimated mass-transfer coefficients gave a value magnitude three orders greater than the measured reaction rates, indicating that process conditions were far from external diffusional limitations. The effects of external mass-transfer resistances were experimentally evaluated by repeating a set of process conditions while employing a different linear velocity. Results of these experiments indicated that conversion was not affected for linear velocity higher than 7 cm/s, within the experimental error. Likewise, estimates of interphase temperature gradients showed fluid–solid differences of less than 1 °C. The possibility of internal pore diffusion was examined by measuring conversions at fixed conditions but varying catalyst particle size. Results showed that pore diffusional resistance was absent for particles less than 1 mm in diameter. Intraparticle mass-transfer resistances were theoretically evaluated by computing effectiveness factors, which were calculated to be greater than 0.98, indicating that intraparticle mass-transfer resistances were not significant. Finally, internal thermal gradients also proved to be negligible over the range of conditions evaluated in this study. The feed flow through the reactor was set at 100 ml/min (linear velocity of 13.3 cm/s), and the gas hourly space velocity (GHSV) was maintained at 30,000 h^{-1}. Feed stream to the reactor was prepared by delivering liquid CB with a syringe pump into dry air, and the injection position was electrically heated to ensure complete evaporation of the liquid reaction feeds. Before the reaction, the catalyst was pretreated in the flow of 10% O_2/N_2 (50 ml/min) for 2 h. For a typical CB oxidation, the reactant feed was composed of 1000 ppm CB and 10% O_2 and N_2 (balance). The temperature of the reactor was measured with a thermocouple located just at the bottom of the micro-reactor. The effluent gases were analyzed online at a given temperature by using gas chromatographs (GC9790, FULI) equipped with a SGE-30QC3/AC5-0.25 capillary column and a flame ionization detector (FID) for the quantitative analysis of the organic chlorinated reactant. Catalytic activity was measured over the range 100–450 °C, and the conversions were calculated by subtracting the outlet concentration from the inlet concentration of the reactant and dividing by the inlet concentration. These conversions were obtained at different temperatures under steady state at each temperature. All the reactions were repeated three times to assure reproducibility. Furthermore, carbon balances could be as accurate as within 5%. The concentrations of Cl_2 were analyzed by the effluent stream bubbling through a 0.0125 M NaOH solution, and chlorine concentration was then determined by the titration with ferrous ammonium sulfate (FAS) using N,N-diethyl-p-phenylenediamine (DPD) as indicator [29]. Here, it should be noted that the total error caused in these chemical analyses may be within ±5%. The concentration of