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Kinetics and mechanism study on catalytic oxidation of chlorobenzene over V_2O_5/TiO_2 catalysts

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ABSTRACT

In this article, we present a detailed study combining the kinetic studies and *in-situ* FTIR experiments to investigate the oxidation behavior of chlorobenzene over V_2O_5/TiO_2 catalysts. The catalytic data show the 3–5 wt.% V_2O_5/TiO_2 catalysts are best fit for the oxidation of chlorobenzene. The calculated apparent reaction orders are about 0.6 and 0.2, respectively. The results of *in-situ* FTIR provided mechanism insights into the catalytic reaction, which supports the following proposal: (i) a nucleophilic substitution on V=O species and (ii) attacking by surface oxygen through a electrophilic substitution, then (iii) followed by the cracking of ring structure, and further oxidation of the resulting species to form final products. The above results further suggest that the nucleophilic substitution process and surface reaction are kinetically significant steps for chlorobenzene oxidation, determining the overall rate of the reaction. Furthermore, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene as additional reactants were tested together with chlorobenzene in binary mixtures to examine their competition reactions.

1. Introduction

In China, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) known as dioxins, that originated from the incineration of municipal and medical waste are drawing more and more attention [1–4]. Adsorption methods, such as utilizing activated carbon (AC) as adsorbent can reduce PCDD/Fs pollutions effectively, but it can only achieve transferring of contaminants, which need further treatments [5]. Catalytic oxidation is able to decompose the pollutants into CO_2, H_2O and other small molecules, achieving complete decomposition [6,7]. Therefore, compared with the traditional adsorption methods, employing catalytic oxidation to control dioxins emissions is a more economical and environmentally friendly way.

Vanadia-based catalysts have been applied industrially, such as V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2, which are commercially employed for the reduction of NO_x known as NH_3-SCR [8,9]. According to previous reports, these catalysts have been also found to be effective and stable for the destruction of chlorine-containing organic compounds, which allows the simultaneous abatement of PCDD/Fs and NO_x from waste incinerators [10–12]. Recently, some authors employed carbonaceous materials to promote the adsorption of pollutants and also O_3 was used to further promote dioxins oxidation [13,14]. However, PCDD/Fs are trace organic pollutants with high toxicity, and it is difficult to study the catalytic properties directly in laboratory scale. Therefore, chlorinated benzenes are generally employed for their structural similarity to PCDD/Fs and less toxicity [15–17]. Krishnamoorthy et al. [18] investigated the catalytic oxidation of 1,2-dichlorobenzene over different transition metal oxides and reported that Cr_2O_3 and V_2O_5 based catalysts have the highest activity, and TiO_2 seems to be the best catalyst support. Bertinchamps et al. [19] studied the catalytic oxidation of benzene over forty different formulations of transition metal oxides based catalysts, and reported similar results. The authors also investigated the effects of a transition metal oxide dopant into V_2O_5/TiO_2 based catalysts toward the catalytic process of chlorobenzene [20].

The catalytic behavior of a reactant is associated with the interaction between the catalyst and the reactant itself. Debecker et al. [21] proposed that the adsorption of furan is significantly different with chlorobenzene, and some of the previously proposed catalyst improvement strategies based on the experiments using chlorobenzene actually prove to be disadvantageous in the removal of PCDD/Fs, which indicates that furan may be a better choice for this purpose [21,22]. Hetrick et al. [23] investigated the

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adsorption and oxidation of *o*- and *p*-chlorophenol over a 3.6 wt.% V_2O_5/TiO_2 catalyst, and found the catalyst to be active at temperatures as low as 200 °C due to a strong adsorption of these species. Although directly using PCDD/Fs as reactants is quite difficult, some precious data in laboratory scale were still reported [11,13,22]. And it seems that the catalytic behavior of PCDD/Fs is close to furan and chlorophenol. But one should also admit that the concentration of these pollutants varies greatly than that of PCDD/Fs, so the rationality of these species as model reactants is still under debate. The differences between these model reactants and PCDD/Fs mainly include variety of functional groups, number of chlorine substituents, molecular weight and concentration in flue gas. Such differences can directly influence the catalytic behavior that obtained in the laboratory scale [11,21–24]. Under this circumstance, understanding the links between microscopic mechanism and macroscopic phenomenon of model reactants becomes very important. These information can not only give explanations to their own catalytic characteristics, but also provide predictions to catalytic macroscopic behavior of PCDD/Fs, especially when the distinction between model reactants and PCDD/Fs can be analyzed. To the best of our knowledge, such studies are still very few even though V_2O_5/TiO_2 based catalysts has been successfully applied in industrial scale.

Therefore, both catalytic (kinetic) studies and *in-situ* FTIR methods are combined to study the oxidation behavior of chlorobenzene in this paper. V_2O_5/TiO_2 catalysts with different vanadia content were prepared, the changes of surface vanadia species were characterized by X-ray diffraction, Raman and *in-situ* FTIR measurements, and kinetic parameters of chlorobenzene oxidation were calculated. According to *in-situ* FTIR experiments, the function of different surface vanadia species was discussed, the transformation of intermediates that formed during catalytic oxidation was studied. Furthermore, 1,2-dichlorobenzene (*o*-DCB), 1,3-dichlorobenzene (*m*-DCB) and 1,2,4-trichlorobenzene (1,2,4-TCB) as additional reactants were tested together with chlorobenzene in binary mixtures to examine their competition reactions. Hence, these results together give a comprehensive understanding related to adsorption, surface reaction and catalytic performance.

2. Experimental

2.1. Catalyst preparation and sample characterization

The V_2O_5/TiO_2 catalysts with different vanadia contents (1, 3, 5, 7 and 9 wt.%, calculated by the weight percentages of V_2O_5) were prepared by wet impregnation method. Commercial P25 TiO_2 (Degussa, >99.5%; 80% anatase and 20% rutile phases) was calcined at 500 °C for 2 h. And NH_4VO_3 (Aladdin, 99.9%) used as V_2O_5 precursor was heated at 80 °C until all NH_4VO_3 was dissolved. P25 TiO_2 was added into NH_4VO_3 solution, and resulting mixture was stirred for 1 h, then all the water was evaporated using a rotary evaporation apparatus. The powder obtained was dried at 110 °C overnight, and calcined in air at 500 °C for 6 h (5 °C/min). Catalyst samples are referred to as VTi-1, VTi-3, VTi-5, VTi-7 and VTi-9 for simplicity.

The weight percentages of V and Ti were measured by an inductively coupled plasma-optical emitting spectrometer (ICP-OES, Optima 5300DV, PerkinElmer). The porous texture was characterized by N_2 adsorption at 77 K in an automatic surface area and porosity analyzer (Autosorb iQ, Quantachrome). The total surface area was calculated from the N_2 adsorption isotherms using the Brunauer–Emmett–Teller (BET) equation and the pore volume was determined from the N_2 desorption isotherms using the Barrett–Joyner–Halenda (BJH) method. The powder X-ray diffraction (XRD) patterns of the sample were recorded on a powder diffractometer (Rigaku D/Max-RA) using Cu Kα radiation (40 kV and 150 mA). The Raman spectra were obtained on a Raman spectrometer (Labram aramis, HORIBA Jobin YUvon). The emission line at 514.5 nm from an Ar^+ laser was focused on the sample under a microscope, and the analyzed spot was 1 μm. The time of acquisition was adjusted according to the intensity of the Raman scattering. The wavenumber values reported from the spectra are accurate to within 2 cm^{-1}. The XPS measurements were collected on a photoelectron spectrometer (ESCALAB 250, Thermo Scientific) using Al Kα (1486.8 eV) radiation as the excitation source (powered at 10 mA and 15 kV).

2.2. Catalytic oxidation of chlorinated benzenes

Catalytic evaluations were carried out in a quartz tube, single-pass fixed-bed micro reactor (4 mm i.d.) with a sieve plate in the middle. The reactor was heated by an electric furnace, and the temperature was monitored through a *K*-type thermocouple next to the sieve plate. Chlorinated benzenes were introduced into the reaction flow through a saturator *via* Ar. The total flow rate of the mixed stream was 100 mL min^{-1} with 10 vol.% O_2 (calculated at atmospheric pressure and room temperature). The entire gas path was wrapped with heating belts and heated to 80 °C in order to reduce adsorption. The analyses of the reactants and organic products were performed on-line by gas chromatography (GC 7890A, Agilent), which was equipped with a flame ionization detector (FID) and an electron capture detector (ECD). The CO_x yields were also determined on-line by gas chromatography (GC-QP2010, Shimadzu), and the detector used was a FID with a methanizer furnace for converting CO_x to CH_4. The HCl selectivity was analyzed by gas detector tubes of HCl and Cl_2 (Cl_2 was never observed in this work). The concentrations of chlorinated benzenes in the mixed steam were calibrated through a by-pass (±1%).

In a typical run, 100 mg of the catalyst (corresponding WHSV of 60,000 mL g^{-1} h^{-1} and GHSV of 37,500 h^{-1}, in the form of 150–180 μm) was placed on the sieve plate. The catalyst was treated at 400 °C for 1 h in a 10% O_2/Ar stream, then the catalytic bed temperature was cooled down to 100 °C (no conversion was observed) and stabilized for 60 min. Subsequently, the catalytic evaluation was carried out with a heating rate of 5 °C/min at a temperature gradient of 25–400 °C and stabilized until a stead state was achieved (defined as less than 2 ppm change in outlet concentration over 30 min). The conversion was calculated by the Eq. (1):

$$x = \frac{\mathrm{C(in)} - \mathrm{C(out)}}{\mathrm{C(in)}} \times 100\% \tag{1}$$

where *x* is the conversion, C(in) and C(out) are the inlet and outlet concentrations of gas-phase chlorinated benzenes. The blank run (without catalyst), which was performed at 100–340 °C, revealed that neither catalytic nor gas-phase homogeneous reactions had occurred.

2.3. Kinetic studies

The external diffusion effect was investigated by varying the speed of feed gas while keeping a constant WHSV (60,000 mL g^{-1} h^{-1}). Similarly, the internal diffusion effect was checked by changing the particle size of the catalyst (as shown in Fig. S1). The results showed that the catalytic reaction was operated without diffusional limitation under 12% conversion of chlorobenzene. The kinetic experiments were carried out under differential condition (the maximum conversion was controlled below 8%). And the reaction rate was calculated as follows:

$$-r = \mathrm{F} \times \frac{dx}{dW} \approx \mathrm{F} \times \frac{x}{W} \tag{2}$$