Effects of metal and acidic sites on the reaction by-products of butyl acetate oxidation over palladium-based catalysts

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ABSTRACT

Catalytic oxidation is widely used in pollution control technology to remove volatile organic compounds. In this study, Pd/ZSM-5 catalysts with different Pd contents and acidic sites were prepared via the impregnation method. All the catalysts were characterized by means of N_2 adsorption-desorption, X-ray fluorescence (XRF), H_2 temperature programmed reduction (H_2-TPR), and NH_3 temperature programmed desorption (NH_3-TPD). Their catalytic performance was investigated in the oxidation of butyl acetate experiments. The by-products of the reaction were collected in thermal desorption tubes and identified by gas chromatography/mass spectrometry. It was found that the increase of Pd content slightly changed the catalytic activity of butyl acetate oxidation according to the yield of CO_2 achieved at 90%, but decreased the cracking by-products, whereas the enhancement of strong acidity over Pd-based catalysts enriched the by-product species. The butyl acetate oxidation process involves a series of reaction steps including protolysis, dehydrogenation, dehydration, cracking, and isomerization. Generally, butyl acetate was cracked to acetic acid and 2-methylpropene and the latter was an intermediate of the other by-products, and the oxidation routes of typical by-products were proposed. Trace amounts of 3-methylpentane, hexane, 2-methylpentane, pentane, and 2-methylbutane originated from isomerization and protolysis reactions.

Introduction

Volatile organic compounds (VOCs), which are widely emitted from industrial processes, are hazardous to the environment and public health. They are organic compounds that can participate in photochemical reactions with nitrogen oxides in the presence of sunlight, thereby producing more toxic compounds (Diaz et al., 2005). Among various kinds of VOCs abatement treatments, catalytic oxidation is considered to be one of the most effective and energy-saving techniques because it can convert VOCs into carbon dioxide (CO_2) and water at low reaction temperatures. Catalysts for the treatment of VOCs are supported noble metals (Bendahou et al., 2008) and transition metal oxides (Saqer et al., 2011; Choudhary and Deshmukh, 2005). The catalytic activity of noble metal-based catalysts is generally higher than that of metal oxides. Palladium (Pd) nanoparticles are especially active for a wide range of VOCs oxidation states (Giraudon et al., 2008). In recent years, studies on catalysts have not only focused on catalysts with superior performance for catalytic oxidation, but also on the reaction processes and mechanisms of VOCs oxidation. Researchers tend to understand the reaction mechanism of catalytic oxidation over Pd-supported catalysts via kinetic models, which include the power-

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rate law model, the Mars-van Krevelen (MvK) model, and the Langmuir-Hinshelwood (L-H) model. Among these models, the MvK model has been widely accepted for VOCs oxidation over Pd-supported catalysts. During the active phase of VOCs oxidation over a Pd-supported catalyst, Pd^{2+} has been proposed to catalyze hydrocarbon oxidation, and Pd^0 can promote the catalytic activity by maintaining a Pd^{2+}-Pd^0 cycle during the dissociation of VOCs. Thus, the reaction rate is accelerated (Nag, 2001). However, the validity of each mechanism strongly depends on the properties of the catalyst (noble metal and nature of the support) as well as the features of the VOCs; thus, the validity is difficult to generalize. A certain amount of incompletely combusted product that is formed during catalytic oxidation is inevitable. Thus, the reaction by-products and processes need to be addressed.

In our previous work, the relation between reaction by-products and the acidity of the catalyst was investigated (Yue et al., 2013). In this article, we selected butyl acetate oxidation, a subject that has not been studied in-depth, to obtain more information about the influence of metal and acidic sites on by-product distribution. Furthermore, we explored the oxidation process by using the thermal desorption/gas chromatography-mass spectrometry GC-MS technique over Pd-supported catalysts.

1 Experimental

1.1 Catalyst preparation

ZSM-5 zeolite (Si/Al = 25, Tianjin Chemical Plant, China) was impregnated in aqueous solutions of $Pd(NO_3)_2$ (0.3 wt%, 0.5 wt% and 1 wt%) to obtain 0.3PdZ, 0.5PdZ, and 1PdZ catalysts, respectively. Pd/γ-Al_2O_3 (99.9%, Alfa Aesar, USA) was prepared using the same impregnation process. Pd/γ-Al_2O_3 was then mixed with pure ZSM-5 to obtain a mixture named MIX (Pd: 0.5 wt%). All samples were dried at 80°C for 24 hr, and calcined at 500°C for 4 hr.

1.2 Catalyst characterization

The N_2 adsorption/desorption isotherms of the catalysts were collected at 77 K using a gas sorption analyzer (NO-VA 1200, Quantachrome Corp., USA). All samples were degassed in vacuum at 300°C for 3 hr before measurement. The total pore volume was estimated from the amount of adsorbed nitrogen at a relative pressure (P/P_0) of about 0.99. The specific surface area (S_{BET}) was calculated using the Brunauer-Emmett-Teller (BET) method. The elemental composition of each sample was analyzed via X-ray fluorescence (XRF) (XRF-1800 spectrometer, Shimadzu, Japan) using a Rh tube as the excitation source.

The H_2 temperature-programmed reduction (H_2-TPR) was performed using a Chemisorb analyzer (ChemiSorb

2720, Micrometrics, USA). The TPR profiles were obtained by passing a 5% H_2/He flow (50 mL/min) through the catalysts (approximately 100 mg), which were previously dried in helium (50 mL/min) at 300°C for 1 hr.

The NH_3 temperature-programmed desorption (NH_3-TPD) was also performed using a Chemisorb 2720 analyzer. Prior to each TPD test, the sample (100 mg) was pretreated in helium (50 mL/min) at 300°C for 1 hr. The samples were then adsorbed with NH_3/He (2%/98%, V/V) to saturate them with NH_3. The catalyst was flushed with He (50 mL/min) at room temperature to remove the physisorbed NH_3. The desorption profile of NH_3-TPD was then recorded from 25°C to 800°C at a heating rate of 10°C/min.

1.3 Activity measurements

The experiments were conducted in a continuous-flow fixed-bed reactor, which consists of a steel tube (6 mm, i.d.) at atmospheric pressure. In each test, 0.3 g of the catalyst (40–60 mesh) was placed into the tube reactor. A gas that contains VOCs was generated by bubbling air through the VOCs saturator, which was further diluted with another airstream before reaching the reaction bed. The total flow rate was kept at 300 mL/min, i.e., a gas hourly space velocity (GHSV) of 30,000 hr^{-1}, with a butyl acetate concentration of 1500 ppm. The reaction temperature was first increased to 100°C as the feed stream passed over the reactor bed and was then stabilized for 30 min. The reaction bed temperature was increased to the following setting and was maintained for 20 min for online detection before performing the next procedure.

Online analysis was performed via simultaneous gas chromatography (GC; model 6820, Agilent, USA) and GC-mass chromatography (MS; Agilent 6890, Agilent, USA). A gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) was employed for quantitative analysis, and GC-MS was used for qualitative analysis. The by-products were collected on a mixed Tenax/carbon tube for several min at each temperature point and then desorbed by a thermal desorber (Unity 2 series, Markes International Ltd., UK) before passing into the GC-MS device.

2 Results and discussion

2.1 Catalyst characterization

The Pd loading, surface area, and total pore volume of the catalysts are listed in **Table 1**. For the Pd-supported catalysts, the percentage of Pd loading increased from 0.09 wt% to 0.40 wt%. The value for 0.5PDZ was similar to that of MIX, which indicates that the Pd contents in these two catalysts were similar. Meanwhile, pure ZSM-5 had a relatively high S_{BET} (346.0 m^2/g), which was larger than