A highly active and anti-coking Pd-Pt/SiO$_2$ catalyst for catalytic combustion of toluene at low temperature

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ABSTRACT

Catalytic combustion has been identified as one of the most efficient and economically feasible routes for removing volatile organic compounds. In this work, supported noble-metal (Pd and Pt) catalysts for catalytic combustion of toluene were prepared by an improved incipient wetness impregnation method. Controlled amounts of oleic acid (OA) were introduced into the aqueous solution of metal salts in this new preparation method, which improved Pd and Pt dispersion remarkably on SiO$_2$, as confirmed by XRD and TEM. XPS results showed that introduction of OA in the catalyst preparation resulted in increased proportion of metallic palladium. All of the activities in catalysts with OA were much higher than those of the catalysts without OA in the same catalyst system. Among the catalysts prepared, the 0.25%Pd-0.25%Pt/SiO$_2$–OA catalyst exhibited the best catalytic activity for toluene oxidation, and the T$_{98}$ of toluene was only 160 °C under the conditions of toluene concentration at 1000 ppm and SV at 60,000 mL/(g h). Furthermore, the 0.25%Pd-0.25%Pt/SiO$_2$–OA catalyst maintained high catalytic activity in the active stability test at 160 °C, and the result of TG indicated that no coke was formed on the spent catalyst.

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1. Introduction

As one of the major components of air pollution, volatile organic compounds (VOCs) are emitted mainly from transportation and industrial processes [1,2]. VOCs are harmful to human health and the environment because of their toxic, malodorous, carcinogenic and mutagenic nature [3]. In addition, they are recognized as a component and promoter of photochemical smog, which is found in many large cities all over the world [4]. Therefore, methods of eliminating VOCs have attracted considerable attention in the light of stringent worldwide environmental legislation. Up until now, a majority of the current industrial VOC abatement has been carried out by catalytic combustion technology, which has been identified as one of the most efficient and economically feasible routes [5–7]. Consequently, the research and development of catalysts for catalytic combustion has become a hotspot research area, internationally [8,9].

The catalysts used for catalytic combustion include mainly perovskites [10,11], transition metal oxides [12–14] and supported noble-metal catalysts [15–19]. Among these, supported noble-metal catalysts are preferred for catalytic combustion, especially

for low-concentration VOCs at low temperature [20–23]. Because of their large surface areas, acidic properties, and high thermal and hydrothermal stabilities, solid acid catalysts such as zeolites, γ-Al$_2$O$_3$, ZrO$_2$ and SiO$_2$ have been extensively considered as catalyst carriers for supported noble-metal catalysts [24–28]. For example, S. Siffert and co-workers prepared Pd/FAU and Pd/BEA, which were found to be powerful catalysts for the total oxidation of VOCs [29]. Montes et al. carefully investigated the activity and stability of Pt/Al$_2$O$_3$ catalysts in the oxidation of toluene [30]. However, the main drawback in using the solid acid catalysts as the catalyst carriers for catalytic combustion is their high tendency toward carbon deposition, resulting in deactivation of the catalysts [31]. First, the acidic sites always participate in coke production as a side reaction. Second, the micropores in solid acid catalysts, especially in conventional zeolites, significantly influence the mass transfer in catalytic combustion. Currently, solid acid catalysts containing hierarchical pores have been synthesized to improve the mass transfer [32,33]. S. Siffert et al. synthesized hierarchical bimodal macro-mesoporous ZrO$_2$ as the carriers for a Pd/ZrO$_2$ catalyst that exhibited high activity for VOCs oxidation [34]. Mesoporous Beta zeolite-supported Pt catalyst was successfully prepared by Xiao et al., and showed superior performance in the catalytic combustion of toluene [35]. Despite the good mass-transfer properties of mesoporous solid acid catalysts, however, carbon deposition still occurred, only at a

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slower rate. Therefore, it is still a challenge to achieve a highly active and stable catalyst for catalytic combustion at low temperature.

Recently, Mo et al. reported a highly active and anti-coking Ni-La$_2$O$_3$/SiO$_2$ (silica gel) catalyst for syngas production from dry CO$_2$ for reforming methane [36]. The preparation process was simple and similar to the traditional incipient wetness impregnation method. Small amounts of oleic acid (OA) were introduced into the aqueous solution of metal salts in this new preparation method, which improved nickel dispersion remarkably. The mechanism of OA also has been investigated in detail by Mo et al.; it can be described as follows [37]. Metal ions and carboxyl of OA can form coordination compounds, which would self-assemble on the metal ion species surface as a shell. The shell could prevent the core (metal ion species) from agglomeration during thermal pretreatment. The new method provided an inspiration, and we would like to design a supported metal catalyst on silica in order to achieve a highly active and anti-coking catalyst for catalytic combustion of VOCs at low temperature. Fumed silica was used as the catalyst support; it is an inexpensive raw material for making zeolites, and can be commercialized for bulk production.

2. Experimental

2.1. Materials

The fumed silica (7 nm particle size, specific surface area: 380 m^2/g) was provided by Evonik Degussa Corp. H-ZSM-5 (15 μm particle size, Si/Al = 25, specific surface area: 340 m^2/g) was provided by Nankai Catalyst Corp. Silica gel (50 μm particle size, specific surface area: 360 ± 30 m^2/g) was provided by Qingdao Kaibang Material Corp. Metal nitrates of AR purity were purchased from Aladdin. H$_2$PdCl$_6$ and H$_2$PtCl$_6$ were supplied by Hangzhou Kaiming Catalyst Corp.

2.2. Catalyst preparation

2.2.1. Monometallic catalyst

The catalysts were synthesized with an improved incipient wetness impregnation method as described in references 36 and 37. Unlike in the traditional incipient wetness impregnation method, oleic acid (OA) was introduced into the aqueous solution of metal salts. The preparation process was as follows. First, 11.8 mg of H$_2$PdCl$_6$ was dissolved in 4 mL of deionized water, and then 14.5 μL of oleic acid (a molar ratio of OA/Pd = 1) was added into the solution. After stirring for a few minutes at room temperature, 1 g of fumed silica was introduced into the above solution. Subsequently, the samples were impregnated at room temperature for 10 h. Then the impregnated catalyst was aged at room temperature for 10 h. After drying out the H$_2$O at 110 °C, the sample was calcined at 550 °C for 4 h. The catalysts prepared with OA and without OA were designated as 0.5%Pd/SiO$_2$–OA and 0.5%Pd/SiO$_2$, respectively. The 0.5%Pt/SiO$_2$, 0.5%Pt/SiO$_2$–OA, 5.0%CuO/SiO$_2$, 5.0%CuO/SiO$_2$–OA, 2.5%Fe$_2$O$_3$/SiO$_2$ and 2.5%Fe$_2$O$_3$/SiO$_2$–OA catalysts were prepared with this new method, using an appropriate amount of aqueous solution of metal salts. Furthermore, the supported noble-metal catalysts were reduced by hydrogen for two hours before catalyst characterization and catalytic activity testing.

2.2.2. Bimetallic Pd-Pt catalyst

First, 5.9 mg of H$_2$PdCl$_6$ and 8.0 mg of H$_2$PtCl$_6$ were dissolved in 4 mL of deionized water, and then 14.5 μL of oleic acid (a molar ratio of OA/Pd + Pt = 1) was added into the solution. After stirring for few minutes at room temperature, 1 g of fumed silica was introduced into the above solution. Subsequently, the samples were impregnated at room temperature for 10 h. After drying out the H$_2$O at 110 °C, the dried sample was calcined at 550 °C for 4 h. The catalysts prepared with OA and without OA were designated as 0.25%Pd-0.25%Pt/SiO$_2$–OA and 0.25%Pd-0.25%Pt/SiO$_2$, respectively. The other Bimetallic Pd-Pt catalysts with various carriers were prepared through a similar process. Furthermore, the supported noble-metal catalysts were reduced by hydrogen for two hours before catalytic activity testing.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained with a RIGAKU Ultimate IV diffractometer using Cu Kα radiation. Thermal gravimetric analysis (TGA) experiments were performed on a Mettler-toledo thermogravimetric analyzer (TGA/DSC LF1600, Switzerland) at the range of room temperature to 700 °C at a heating rate of 20 °C/min at atmospheric pressure under air atmosphere. The flow rate of the air was 40 mL/min. Transmission electron microscopy (TEM) experiments were performed on a JEM-2100 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. Nitrogen sorption isotherms at −196 °C were measured using an Autosorb-iQ system (Quantachrome Instruments). The surface area was calculated by using the Brunauer–Emmett–Teller (BET) method. The pore size distribution was calculated by using the Barrett-Joyner-Halenda (BJH) method. X-ray photoelectron spectra (XPS) of the samples were recorded using a Thermo Scientific ESCALAB 250Xi with Al K X-ray radiation for the X-ray source. The binding energies (BEs) were calibrated against C1s (284.8 eV) peaks. The samples were all reduced by H$_2$ before catalyst characterization of XRD, TEM, BET and XPS. Catalysts were stored in sealed bags and not re-activated prior to XPS measurements. Temperature-programmed desorptions of toluene (toluene-TPD) were performed on a gas chromatograph (Kexiao, GC1690) equipped with a flame ionization detector (FID). In a typical run, 100 mg of sample were pre-treated in a H$_2$ flow (30 mL/min) at 300 °C for 2 h and then cooled down to 20 °C prior to the adsorption of toluene for 2 h. After saturation with toluene, the sample was flushed with pure N$_2$ (30 mL/min) for 2 h at 20 °C. The profiles of toluene-TPD were recorded online at a heating rate of 10 °C/min until 800 °C. The chemisorption of CO was performed on a chemisorption analyzer (micromeritics Auto Chem II). In a typical run, 100 mg of sample were pre-treated in a H$_2$ flow (30 mL/min) at 400 °C for 1 h and then cooled down to 50 °C prior to the adsorption of CO pulses.

2.4. Catalytic activity tests

The catalytic combustion of toluene experiment was carried out in a fixed-bed quartz reactor (i.d. 6 mm and length 300 mm) at atmospheric pressure. The catalytic combustion of toluene over noble metal catalyst was performed at the temperatures between 140 and 210 °C. The experiment over transition metal catalyst was performed at the temperatures between 300 and 400 °C. The typical experiment used 100 mg of catalyst (40–60 mesh) with a total flow rate of the feed stream at 100 mL/min, giving a space velocity (SV) of 60,000 mL/(g h). The feed stream containing 1000 ppm toluene was generated by bubbling air through a gas washing bottle containing pure toluene chilled in an ice-water isothermal bath, and then further diluted with another air stream. Fig.S1 shows the experimental setup for the combustion of toluene. Prior to the catalytic reaction, the supported noble-metal catalyst was reduced in an H$_2$ atmosphere at 300 or 400 °C for 2 h. (The supported transition metal oxide catalyst was pretreated in an N$_2$ flow at 400 °C for 2 h.) The concentration of the toluene at the outlet of the reactor was monitored with a gas chromatograph (Kexiao, GC1690) equipped with a flame ionization detector (FID). The concentration of the oxidative products (CO$_2$ and CO) was monitored with a gas chromatograph