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Article

Effect of preparation method on the performance of Pd-MnO_x/γ-Al₂O₃ monolithic catalysts for ground-level O₃ decomposition



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ABSTRACT

MnO_x+γ-Al₂O₃ and MnO_x/γ-Al₂O₃ catalysts were prepared by the sol-gel and sequential precipitation methods, respectively. The same amount of Pd was loaded on these catalysts by incipient wetness impregnation. The two Pd-MnO_x/γ-Al₂O₃ catalysts with different physicochemical properties were coated on cordierite. The catalysts were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, H₂ temperature-programmed reduction, and N₂ adsorption-desorption measurement. The preparation method and calcination temperature of MnO_x have significant impact on the crystalline phase of MnO_x, MnO_x species and active oxygen species, and textural properties of the catalysts. The experimental results showed that 0.60 μL·L⁻¹ of ozone was completely decomposed on these catalysts in the temperature range of 16 to 90 °C at space velocities from 380000 to 580000 h⁻¹. In particular, the activity for O₃ decomposition was excellent on the Pd/MnO_x+Pd/γ-Al₂O₃ catalyst that used MnO_x prepared by the sol-gel method. Mnⁿ⁺ is beneficial for O₃ decomposition, and Mn²⁺, Mn³⁺, and Mn⁴⁺ were presented in a mole ratio of 1.7:1:3 on the surface of the catalyst.

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1. Introduction

Ground-level O₃ is formed from reactions under ultraviolet light between VOCs and nitrogen oxides (NO_x) released from automobile exhaust gas and power plants [1–3]. Modern office equipments such as photocopier machines, laser printers, and air conditioners also produce O₃. These break the tropospheric ozone cycle equilibrium and result in the increase of O₃ concentration and the variation of ground-level temperature [4,5]. O₃ is highly injurious. 0.1 μL·L⁻¹ O₃ causes severe health problems like headaches, respiratory illness, throat irritation and damage to mucous membranes [6] to humans, and increases cardiovascular mortality [7]. Photochemical smog aerosol formed by O₃ is atmospheric pollution and the resulting low

visibility result in an increase in traffic accidents. Woody plants including arbor and shrubs are subjected to damage by ambient O₃ [8]. The typical symptoms of foliar injury are dark stipple, mottling and tip burn. O₃ is also an important air pollution in Europe and North America [9].

According to Occupational Safety and Health Administration regulations, the threshold level for allowable exposure is 0.1 μL·L⁻¹ during a 8 h period [10]. The allowable concentration in the working environment is 0.1 μL·L⁻¹ in Japan [11]. In March 2012, the State Environmental Protection Administration of China promulgated the ambient air quality standard regulation GB3095-2012 that the O₃ average concentration must be lower than 0.046–0.075 μL·L⁻¹ in 8 h, and it will be enforced in January 2016. Therefore, the catalytic decomposition of ground-

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level O_3 is an important area of research from the point of view of environment and health. It is necessary and urgent that high activity catalysts are found for ozone abatement [12,13].

Challapalli et al. [14] investigated the catalytic decomposition of O_3 over activated carbons (AC). A “high activity” for O_3 decomposition was observed, which was mainly due to the chemical interaction of O_3 with activated carbon. This interaction resulted in the formation of oxygen-containing surface groups on the activated carbon until saturation. Then, the conversion sharply decreased and the AC gave “low activity”. The catalytic decomposition of O_3 was not steady over the activated carbon. Zhang et al. [15] reported that the surface carbon of the Au/AC catalyst was partly oxidized after O_3 decomposition. Some researchers found that MnO_2 was the most active among the transition metal oxides for O_3 decomposition [10,16,17]. Dhandapani et al. [10] showed by temperature-programmed reduction (TPR) that MnO_2 was more reducible than the other oxides. Kameya et al. [18] studied MnO_2 impregnated Pd for the decomposition of O_3 in high humidity. The activity of the catalyst was higher than other existing catalysts. Wu et al. [19] showed that a Pd catalyst demonstrated not only the highest O_3 conversion efficiency among the catalysts tested (Pt, Pd, Pd/Ni, and Ni), but also it had strong resistance to water vapor, which inhibited O_3 decomposition reaction at low temperatures. In addition, Zhou et al. [12] observed that a synergetic effect took place between Pd and MnO_x when O_3 was decomposed on the surface of Pd/ MnO_x + Pd/ γ - Al_2O_3 catalysts. Pd was both resistant to humidity and an active species.

Pd/ MnO_x catalysts were investigated in our group in recent years [12,20,21], where it was shown that $0.6 \mu\text{L}\cdot\text{L}^{-1}$ of O_3 was completely decomposed at ambient temperature over these catalysts. $MnCO_3$ was calcined and decomposed to MnO_x ($x = 0.16\text{--}2$), and then transformed to Mn_2O_3 with increasing calcination temperature [20]. The results showed that mixed phases of $MnCO_3$ and MnO_x had better catalytic activity. Pan et al. [21] showed that MnO_x was prepared by a chemical reaction of $Mn(NO_3)_2$ and urea. The $MnCO_3$ intermediate was gradually transformed to MnO_2 and Mn_2O_3 with the increase of calcination temperature. They displayed that mixed phases of MnO_2 and Mn_2O_3 have better catalytic activity. The investigations of Yu et al. [20] and Pan et al. [21] revealed that mixed phases of MnO_x had better activity. Zhou et al. [12] confirmed that the activity of mixed phases of a MnO_x catalyst was better than that of a MnO_2 catalyst. Although the prepared catalysts contained Pd, we focused on discussing the MnO_x active species in this paper. The MnO_x was prepared by the sol-gel and sequential precipitation methods. The aim was to study the effect of the preparation method and calcination temperature on the phase of MnO_x , and the specific surface area and electronic characteristics of the surface of the catalysts and their catalytic activity.

2. Experimental

2.1. Preparation of catalysts

The preparation of γ - Al_2O_3 was given in Ref. [12]. Manganese acetate (West Sichuan Chemical Company, AR)

and citric acid (Chongqing Oriental Reagent Factory, AR) were mixed in a molar ratio of 1:1 and the solution was adjusted to pH 8.5 by $NH_3\cdot H_2O$ under vigorous stirring at 70°C to form a sol. The sol was kept overnight and then heated at 70°C for 3 h in a water bath to eliminate the solvent. The resulting viscous gel was dried at 110°C for 12 h, then crushed into a fine powder. The dried powder was divided into four parts which were heated in a muffle furnace for 4 h at 300, 400, 500, and 600°C , respectively. The MnO_x samples were obtained. In addition, a mixture of the MnO_x and γ - Al_2O_3 in a mass ratio of 4:1 was ball-milled with distilled water, and then was dried at 110°C for 6 h to prepare the $MnO_x + \gamma$ - Al_2O_3 .

An aqueous solution of $Al(NO_3)_3$ (Chongqing Southern China inorganic reagent factory, AR) was adjusted to pH 9 by $NH_3\cdot H_2O$ with vigorous agitation. An $Al(OH)_3$ precipitate was formed. Then 50% $Mn(NO_3)_2$ and $NH_3\cdot H_2O$ were added dropwise into the $Al(OH)_3$ precipitate at pH 9 under vigorous stirring. The final precipitate was aged at 70°C for 3 h, filtered off, washed with distilled water, and dried at 110°C for 12 h. After that, the dried powder was divided into four parts and calcined for 6 h at 300, 400, 500, and 600°C , respectively. MnO_x/γ - Al_2O_3 powder containing MnO_x 80% and γ - Al_2O_3 20% was obtained.

The Pd catalysts were prepared by wet impregnation. The loading of Pd was 1.6 wt% for all of the samples. (1). An amount of an aqueous solution of $Pd(NO_3)_2$ (Chengdu Guangming Equipment Company, AR) was impregnated in the MnO_x prepared by the sol-gel method and γ - Al_2O_3 in a mass ratio of 4:1. Then, the Pd/ MnO_x and Pd/ γ - Al_2O_3 powder catalysts were mixed together. (2). An amount of an aqueous solution of $Pd(NO_3)_2$ was impregnated in the MnO_x/γ - Al_2O_3 prepared by the sequential precipitation method. (3). An amount of an aqueous solution of $Pd(NO_3)_2$ was impregnated in γ - Al_2O_3 . After impregnation, the Pd/ MnO_x +Pd/ γ - Al_2O_3 , Pd/ MnO_x/γ - Al_2O_3 , and Pd/ γ - Al_2O_3 catalysts were dried at 120°C overnight, and then calcined at 200°C for 3 h in air.

The above powder was ball-milled with distilled water to form a slurry. The slurry was coated onto a cordierite substrate of 0.28 cm^3 (Coring Corporation in American, 400 pore-inch⁻², diameter 5 mm, length 14 mm) and excess slurry was blown off. The catalyst was dried at 110°C overnight and calcined at 200°C for 3 h in air to obtain the Pd/ MnO_x +Pd/ γ - Al_2O_3 , Pd/ MnO_x/γ - Al_2O_3 , $MnO_x + \gamma$ - Al_2O_3 , MnO_x/γ - Al_2O_3 , and Pd/ γ - Al_2O_3 catalysts. The loading of catalyst on the cordierite substrate was $350 \text{ g}\cdot\text{L}^{-1}$.

2.2. Catalyst characterization

H_2 -TPR was carried out using an automated instrument. In a typical experiment, 100 mg of sample was loaded in a U-shaped quartz microreactor. The sample was heated from room temperature to 550°C at a heating rate $10^\circ\text{C}\cdot\text{min}^{-1}$ in a flowing 5% H_2/N_2 mixture gas ($30 \text{ cm}^3\cdot\text{min}^{-1}$). Hydrogen consumption was monitored using a thermal conductivity detector. The XRD analysis was conducted on DX-1000 X-ray diffractometer using $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at 40 kV and 25 mA. The X-ray diffraction (XRD) data were recorded for 2θ values from 10° to 80° at a scan $0.05^\circ/\text{s}$. X-ray photoelectron spectra (XPS)

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