Charcoal-supported catalyst with enhanced thermal-stability for the catalytic combustion of volatile organic compounds

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ABSTRACT

In this study, charcoal powder originated from thinned wood was selected as the support material, and transition metals were used as the catalytic active phases to prepare a series of the charcoal-supported catalysts for the catalytic oxidation of volatile organic compounds. We found that the waste wood derived charcoal with poor thermal-stability could be converted into highly active and durable VOCs elimination catalyst in one-step. The addition of transition metal followed by a thermal-treatment in He (at 1000–1400 °C) significantly improved the thermal-stability of charcoal. Co gave the best promotion effect among the tested metals (Co, Ni, and Fe). The transition metals could not only facilitate the transformation of amorphous carbon structure into graphitic structure during the preparation of the support but also serve as an active phase in the VOCs oxidation reaction. When a charcoal-supported Cu-Co bimetallic catalyst was subjected to the toluene catalytic oxidation, the complete oxidation of toluene was achieved at 237 °C, which was far lower than the thermal resistance temperature of the catalyst (350 °C). Especially, in the ethyl acetate catalytic oxidation, the Cu-Co bimetallic catalyst gave an excellent activity that is slightly superior to a Pt/Al_2O_3 catalyst.

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1. Introduction

In recent years, volatile organic compounds (VOCs) have contributed significantly to air pollution [1]. The control of their emissions has therefore become imperative. Since the environmental legislations all over the world are imposing stringent standards on VOCs emissions, efficient technologies for the removal of VOCs must be developed. Nowadays, there are numerous different methods for removing VOCs such as adsorption, thermal oxidation and catalytic oxidation. Thermal oxidation was one of the most effective means for the VOCs elimination, but it usually proceeds at high temperatures (≥800 °C) and would result in the formation of some hazardous compounds (dioxins, carbon monoxide, nitrogen oxides, etc.) which were even more dangerous than the ones to be eliminated [2]. The catalytic oxidation could achieve a similar effect at a much lower temperature, which made it a more attractive and efficient way in practical utilities.

Noble metal-based catalysts (Pt, Pd, Rh etc.) exhibit high activity and selectivity at low temperature [3–5], but they are unstable in the presence of chloride compounds [6]. Especially with respect to the cost and availability of most noble metals, the use of these catalysts in commercial applications of large-scale involves economic limitations. Transition metals such as Cu, Co, Ni, Fe, Mn, etc. were widely investigated as the alternative to noble metals in the VOCs catalytic oxidation [1,7–11]. Comparing with noble metal-based catalysts, transition metal-based catalysts are generally less active but more resistant towards chloride poisoning. Their costs are also significantly lower, which make them especially suitable for the mass production and application. The activity of transition metals based VOCs catalysts could be enhanced via using appropriate supports. Conventional metal oxides such as Al_2O_3, CeO_2, TiO_2, SiO_2, or mixed oxides (e.g. MnO_x—CeO_2 [12], Co_3O_4—CeO_2 [13]) have been extensively studied and used as catalyst support for eliminating VOCs emission. Recently, carbonaceous support has received increased attention as an alternative to the conventional support, due to its superiority in economic, secure and environmental aspects. Some researchers have revealed favorable

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catalytic activity attained over carbonaceous support catalysts such as activated carbon [1,7,11,14,15] and graphitic carbon [16,17]. Zhang et al. [15] examined the effectiveness of the Pt/AC for the oxidation of VOCs at temperatures below 200 °C. The activity of Pt/AC for benzene oxidation was found to be superior to that of Pt/alumina, in particular under humid conditions. A comparison of alumina-supported transition metal catalysts (Co, Fe, Ni, and Cu) with AC-supported catalysts reported by Lu et al. [1] showed that the conversion efficiency of alumina-supported catalysts was lower than the AC-supported catalysts.

Despite the enhancement of activity by applying carbonaceous materials as support, there are still potential risks in practical utilities. A temperature around 300 °C (or higher) is generally required to completely oxidize VOCs over the AC-supported transition metal catalysts [1,7,11]. The temperature of 300 °C is a potential hazard to the thermal-stability of the AC based catalyst, because activated carbon support in the catalysts can be oxidized by oxygen at this temperature and results in serious catalyst degradation. Furthermore, from a practical viewpoint, the potential temperature rise of the catalytic bed in a VOCs combustor caused by the adiabatic temperature rise cannot be neglected since the VOCs catalytic oxidation is exothermic, which might aggravate this safety hazard. Graphitic carbons are stable under elevated temperatures, but the synthesis of graphite with high surface area is complex and the preparation conditions are uneconomical and severe, in particular, the extremely high temperature (ca. 30000 °C) [17–20]. For example, Zhang et al. [20] reported a preparation of graphitized porous carbon microspheres by the spray drying technique using carbon black nanoparticles as the primary carbon resource. The graphitization treatment was conducted at 2800 °C. Besides, commercially available graphite flakes are usually of small surface area, which makes it unsuitable to be used directly as supports for catalyst. It is highly preferred to enhance the thermal-stability of carbonaceous supports under mild conditions.

In this study, in order to utilize efficiently waste wood (e.g. thinned wood), a charcoal powder derived from thinned wood was selected as the support material, and transition metals were used as the catalytic active phases to prepare a series of charcoal-supported catalysts for the VOCs catalytic oxidation (model VOCs: toluene and ethyl acetate). In order to enhance the thermal-stability of charcoal, a thermal treatment was conducted under mild temperature range (1000–1400 °C), which was far lower than the commercial graphitization temperature of ca. 3000 °C [17–20]. We found that the addition of transition metal followed by a thermal-treatment in He (at 1000–1400 °C) significantly improved the catalyst thermal-stability. Co gave the best promotion effect among the tested transition metals (Co, Ni, and Fe). When a charcoal-supported Cu-Co bimetallic catalyst was subjected to the toluene catalytic oxidation, the complete oxidation of toluene was achieved at 237 °C, which was far lower than the thermal resistance temperature of the catalyst (350 °C). Especially, in the ethyl acetate catalytic oxidation, the Cu-Co bimetallic catalyst gave a dramatic activity comparable and even slightly superior to a Pt/Al_2O_3.

2. Experimental

2.1. Catalyst preparation

A charcoal powder derived from thinned wood (BET surface area = 69.4 m^2/g, supplied from Japan Interaction in Science & Technology Forum) was used as the support material, designated C(raw). Table 1 shows the composition of charcoal ash. Raw charcoal was added into an aqueous solution of cobalt (iron, nickel) nitrate under ambient conditions and the weight ratio of the added metallic element to charcoal was controlled to 20/80. The solution was maintained at room temperature for 2 h under vigorous stirring. After a vacuum drying, the sample was dried in air at 120 °C for 12 h. The dried samples were crushed and sieved into 30–40 mesh. In the subsequent thermal-treatment, the powder sample was heated to different temperatures (1000–1400 °C) in 100 mL/min He (at a ramping rate of 10 °C/min), and maintained at the same temperature for 3 h. In this paper, these samples were denoted as M-C(Hex) (where M = Co, Fe, Ni; He = Helium; x = the thermal-treatment temperature). In order to decrease the preparation cost, a pre-treatment of vacuum desorption was not conducted ahead of the He thermal-treatment. Additionally, some thermal-treated samples were further calcined in air at 350 °C for 3 h, denoted as M-C(Hex, Air350).

After a He thermal-treatment at 1000–1400 °C, ca. 25–28% weight loss was observed over the raw charcoal, which should be attributable to the adsorbed water or oxygen on the charcoal surface and/or in-volatile organic compounds remaining in the meso- and/or micro-pores of the raw charcoal.

The Co-C(He1400, Air350) was used to prepare a catalyst sample with the Cu addition, designated Cu/Co-C(He1400, Air350). The Co-C(He1400, Air350) powder was immersed into an aqueous solution of copper nitrate at room temperature for 2 h, followed by a vacuum drying. Subsequently, the resulted sample was dried at 120 °C for 12 h and then calcined at 350 °C for 3 h in air.

As catalyst control, a graphite powder (070-01325, Wako Pure Chemical Industries, Ltd.), an alumina powder (90928, Soekawa Chemical Co., Ltd.) and an activated carbon powder (037-02115, Wako Pure Chemical Industries, Ltd.) were used in this paper. An alumina-supported Pt (or Co) catalyst was prepared by impregnating alumina in a H_2PtCl_6 (or $Co(NO_3)_2$) solution. After impregnation, the samples were dried naturally for 4 h and then calcined at 500 °C for 3 h in air. Resulted catalysts were designated Pt/Al_2O_3 and Co/Al_2O_3, respectively. Co loading in Co/Al_2O_3 is 20.6 wt%. Pt/Al_2O_3 has a Pt loading of 2.2 wt% with a Pt dispersion of 28.5%. The Pt dispersion was determined by the CO-pulse adsorption method, where pre-treatment conditions were set at 100 °C for 30 min in 70 mL/min He, and then at 400 °C for 30 min. Sample reduction was conducted at 400 °C in 70 mL/min H_2 for 1 h. Finally, the sample was cooled in He. The Pt dispersion was calculated based on the amount of adsorbed CO and assuming adsorption stoichiometry CO:Pt = 1:1. An activated carbon-supported Co catalyst (Co/AC) was prepared by immersing the activated carbon in a $Co(NO_3)_2$ solution at room temperature. After a vacuum drying, the sample was dried at 120 °C for 12 h and then calcined at 300 °C for 3 h in air. Co loading in Co/AC is 19.2 wt%.

The preparation conditions of catalysts used in this paper are summarized in Table 2.

2.2. Catalyst characterization

Powder XRD analyses of the samples were obtained using an X-ray diffractometer (RAD-II C, Rigaku Corp.) with nickel-filtered Cu-Kα radiation. BET specific surface area was determined using the nitrogen adsorption method (SA3100, Beckman Coulter, Inc.). Metal loading was determined using an inductively coupled plasma spectrometer (ICPS-7510, Shimadzu Corp.). Table 2 shows the result of the ICP analysis obtained over different samples.

Thermogravimetric analyses were performed on a TGA-51 (Shimadzu Corp.). In this study, two methods were used to conduct TG analysis: dynamic TG and stationary TG. In the dynamic TG analysis, the sample was pre-treated in 50 mL/min air at room temperature for 30 min and then at 120 °C for 1 h. Subsequently, the sample was heated to 1000 °C in 50 mL/min air at a ramping rate of 10 °C/min, while the weight change was continuously monitored using a thermo-balance. The sample weight relative to the stable value after the 120 °C pre-treatment was used in this paper, i.e. rel-