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Catalytic combustion of volatile organic compound over spherical-shaped copper–manganese oxide

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ABSTRACT

Amorphous spherical-shaped copper–manganese oxide for the catalytic combustion of benzene were successfully obtained by a wet granulation process under different calcination temperatures. The low-temperature (400 °C) calcined catalysts—which showed a larger BET specific surface area, low temperature reducibility, and an amorphous phase—were more active for the catalytic combustion of benzene than the high-temperature calcined catalyst which underwent the amorphous to crystalline phase transition. The catalytic activity tests, depending on the operating parameters, suggested that amorphous spherical-shaped copper–manganese oxide have potential applications for remedying VOC pollution.

Introduction

Volatile organic compounds (VOCs) are major contributors to photochemical smog and are dangerous for the human body [1]. Reducing pollutant concentrations, especially in communities and cities with high-density populations, requires the implementation of control technologies to eliminate or transform them [2,3]. Several techniques are available for the reduction of VOCs, such as adsorption, condensation, incineration, catalytic combustion, and bio-filtration [4–8]. Of these, catalytic combustion appears to be the most promising technology when the VOCs are seldom recycled or exist in low concentration. Catalytic combustion also requires a relatively low temperature, typically under 400 °C, and generates a smaller amount of by-products when compared to incineration [9].

The catalytic combustion of VOCs has been studied using noble metals and transition metal oxides. The noble metals, such as platinum, palladium, and rhodium [10–12], are perfectly active at relatively low reaction temperatures, but they are very expensive and undergo poisoning by chlorinated compounds in the gas stream, which limits their actual field application [4,13–16]. On the other hand, transition metal oxides, such as CuO_x [17–19], MnO_x [9,17,2–25], CeO_x [22,26–29], NiO_x [20,22,25], and their binary mixtures [17,18,28,30,31], could represent alternative choices as commercially available catalysts for VOC removal due to their low cost, good reducibility, high resistance to poisoning, and requirement for a relatively lower operation temperature compared to noble metal catalysts [1,18].

Among the transition catalysts, a copper–manganese (Cu–Mn) oxide shows high performance in the catalytic combustion of various VOCs [4,20,22,24–26,29]. For example, Chen et al. [32] synthesized mesoporous Cu–Mn hopcalite catalysts and reported good catalytic activity for removing ethylene from a carbon dioxide stream. Morales et al. [33] reported that a Cu–Mn bimetallic oxide prepared by a co-precipitation method had an excellent catalytic performance for eliminating ethanol and propane. In these Cu–Mn catalyst systems, catalytic activity was strongly affected by the transition of the catalyst from an amorphous to a crystalline phase [32].

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According to the literature, a more effective oxidation reaction is obtained with an amorphous phase Cu–Mn oxide than crystallized Cu–Mn oxide [32,33]. This can be explained by the high catalytic activity in the oxidation reaction that originates from the redox reaction in the form of $Cu^{2+} + Mn^{3+} \rightleftharpoons Cu^{+} + Mn^{4+}$, which results in electron transfer between the copper and manganese cations within the spinel lattice [32,34,35]. However, the crystalline phase has an enrichment of Cu^{+} and Mn^{4+} on the surface, which has been suggested to result in deactivation of catalysts [32,34,35]. Buciuman et al. [36] claimed that the amorphous phase of Cu–Mn oxide is more active than the crystallized $CuMn_2O_4$ spinel, since the catalytic activity of Cu–Mn oxides was affected by the spillover model, with manganese oxide acting as an oxygen donor and copper oxide as the oxygen acceptor. Therefore, control of the solid structure of a Cu–Mn oxide catalyst becomes very important for VOC removal.

The shaping process is another issue that affects the effectiveness of Cu–Mn oxide catalysts for catalytic combustion of VOCs. Powder-type catalysts are difficult to handle and cause large pressure drops as well as a problems with heat transfer in the system [37]. For these reasons, the powder-type materials require an additional shaping step, with a minimal change in physical and chemical properties, to fulfill the requirements of commercial processes. In general, shaping processes are usually conducted using a press or an extrusion method [38]. After these shaping processes, the BET specific surface area decreases dramatically, and some pores are blocked, which leads to a decline in textural characteristics [38]. Previous studies that have compared the shaping processes for spherical-shaped granules and pellets have indicated that better textural properties are obtained with spherical-shaped granule synthesized by a wet granulation process than with pellet shapes obtained by a press or extrusion methods [37,38]. The BET specific surface area of pellet type materials was significantly decreased due to blocked pores, which reduced adsorption capacity, whereas the spherical-shaped granules formed using a wet granulation method avoided this decrease in the ratio of BET specific surface area [37,38].

In the present study, amorphous spherical-shaped copper–manganese oxide granule was prepared using a wet granulation process. The resulting catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction with hydrogen (H_2-TPR), and N_2 adsorption–desorption measurements. The effect of the Cu–Mn oxide structure, such as amorphous or crystalline structure, was investigated by calcination treatment at various temperatures and the influence of the structure on the catalytic properties was examined for these catalysts.

Experimental

Catalyst preparation and characterization

Preparation of the spherical-shaped copper–manganese (Cu–Mn) oxide granules

The spherical-shaped Cu–Mn oxide granules were prepared using the wet granulation method. An amount (1000 g) of Cu–Mn oxide powder (CuMn(P), PureSphere, Purelyst MD-101) was mixed with a silica sol (Ludox, AS-40 colloidal silica, 40 wt.%) solution and microcrystalline cellulose (Merck, microcrystalline cellulose) using a mixing granulator (Gebrüder Lödige, Maschinenbau GmbH, D-33102). The prepared sample was then dried at room temperature for 6 h to remove water from the granules. This dried sample which contains 15 wt.% of SiO_2 as an inorganic binder was denoted as CuMn(G)25-15. Several CuMn(G)25-15 samples were then calcined at various temperatures (i.e., 400, 500, and 600 °C) for 5 h; the spherical-shaped Cu–Mn oxide granules calcined at these temperatures were designated as CuMn(G)400-15, CuMn(G)500-15 and CuMn(G)600-15, respectively. Catalysts denoted as CuMn (G)400-5, CuMn(G)400-10, CuMn(G)400-15, and CuMn(G)400-20 were also prepared with SiO_2 contents of 5, 10, 15, and 20 wt.%, respectively and calcined these at 400 °C for 5 h.

Characterization of the spherical-shaped copper–manganese (Cu–Mn) oxide granules

The XRD patterns of the catalysts were measured on a Rigaku Ultima IV instrument using Cu Kα radiation at a diffraction angle (2θ) range of 10–80°. The BET specific surface area (S_{BET}) and total pore volume (V_t) were measured by N_2 physisorption at 77 K (TristarII, Micromeritics). The H_2-TPR was measured using a chemisorption analyzer (Autochem II, Micromeritics) equipped with a thermal conductivity detector. The H_2-TPR analysis was conducted on 10 mg of spherical-shaped Cu–Mn oxide granules that were previously pretreated at 150 °C for 1 h in the presence of argon (Ar) before reduction. The reduction gas was a 10% (v/v) mixture of H_2 balanced with Ar, with a flow of 10 mL/min, and the catalyst was heated from 50 to 800 °C (ramp rate: 5 °C/min). The XPS measurements were performed on an AXIS NOVA (KRATOS) probe apparatus using a band-pass energy of 160 eV. The compressive strength was measured using the compressive strength meter shown in Supplementary Fig. S1. One unit of the catalyst was placed on the instrument and the force was vertically applied to the catalyst until the catalyst was broken.

Catalytic activity tests

The catalytic activity tests were performed at atmospheric pressure in a fixed-bed reactor (a 50 cm long and 10 mm I.D. stainless steel cylinder), which was loaded with 2 g of spherical-shaped Cu–Mn oxide granules. The reactant gas was a mixed gas containing 50, 100, 150, 300, and 500 ppm benzene in air. The total flow of the reactant mixture was controlled by a mass flow controller. The temperature was decreased from 390 °C to 120 °C and was maintained for 2 h at each set temperature for stabilization. The concentration of benzene in the effluent gas was analyzed with a gas chromatograph (Agilent J&W, GC Columns 123-503B) equipped with a flame ionization detector. A schematic of the experimental setup is given in Fig. 1.

The three samples with different contents of inorganic binder (i.e., CuMn(G)400-10, CuMn(G)400-15, and CuMn(G)400-20) were tested at a constant gas hourly space velocity (GHSV) of 10,000 h^{-1} to verify the effect of inorganic binder contents. The effect of calcination temperature was examined using CuMn(G) 400-15, CuMn(G)500-15, and CuMn(G)600-15 at a space velocity of 10,000 h^{-1}. The CuMn(G)400-15 catalyst was also used to test the stability of catalysts and operating conditions such as GHSV (10,000, 25,000, and 50,000 h^{-1}). A stability test of the catalysts was carried out using the same equipment as shown in Fig. 1. The catalyst bed was heated to 270 °C (a temperature at which complete benzene oxidation was achieved) and maintained constant at this temperature for 30 min, followed by a decrease to room temperature. This procedure was repeated 10 times to evaluate the stability of the granulized catalysts.

The conversion of benzene ($X_{benzene}$, %) was calculated as follows:

$$X_{benzene}(\%) = \left(1 - \frac{C_{benzene(out)}}{C_{benzene(in)}}\right) \times 100$$

where $C_{benzene}$ (in) and $C_{benzene}$ (out) are the concentrations of benzene in the inlet and outlet gases, respectively.

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