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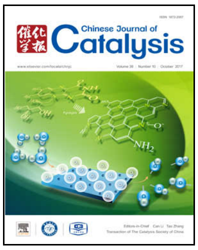

Article

A novel process of ozone catalytic oxidation for low concentration formaldehyde removal

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ABSTRACT

To reduce energy costs, minimize secondary pollution from undecomposed ozone, and improve the efficiency of ozone use, a novel process of cycled storage-ozone catalytic oxidation (OZCO) was employed to remove formaldehyde (HCHO) at low concentrations in air. We applied Al_2O_3-supported manganese oxide (MnO_x) catalysts to this process, and examined the HCHO adsorption capacity and OZCO performance over the MnO_x catalysts. Owing to the high dispersion of MnO_x and low oxidation state of manganese, the MnO_x/Al_2O_3 catalysts with a manganese acetate precursor and 10%-Mn loading showed good performance in both storage and OZCO stages. The presence of H_2O led to a decrease of the HCHO adsorption capacity owing to competitive adsorption between moisture and HCHO at the storage stage; however, high relative humidity (RH) favored complete conversion of stored HCHO to CO_2 at the OZCO stage and contributed to an excellent carbon balance. Four low concentration HCHO storage-OZCO cycles with a long HCHO storage period and relatively short OZCO period were successfully performed over the selected MnO_x/Al_2O_3 catalyst at room temperature and a RH of 50%, demonstrating that the proposed storage-OZCO process is an economical, reliable, and promising technique for indoor air purification.

1. Introduction

Indoor air quality has become a serious issue owing to the increasing amount of time people spent indoors. Formaldehyde (HCHO) is a common volatile organic compound (VOC) presence in indoor air, which poses serious risks to human health [1,2]. Thus, removal of indoor HCHO has attracted considerable attention in the field of environment protection. Various methods of air purification, including catalytic oxidation [3–5], photocatalytic oxidation [6,7], and plasma oxidation [8,9] have been investigated for elimination of HCHO from air. However, considering the low concentration and long-term release of HCHO in indoor environments, most air purification methods are unsuitable for practical applications to indoor HCHO removal owing to their high operating temperatures and requirements for expensive noble metals [10–12].

Recently, ozone catalytic oxidation (OZCO), which involves reactions between active species from ozone, such as active

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oxygen atoms and hydroxyl radicals, and adsorbed VOCs can readily proceed at room temperature without the use of noble metal catalysts. This method is regarded as a promising alternative technique for low temperature oxidation of VOCs [13–15]. Great efforts have been devoted to the elimination of benzene [16–18], toluene [19,20], and formaldehyde [21] by the OZCO approach. In our previous work, we demonstrated that ozone can completely oxidize HCHO into CO_2 and H_2O over a manganese oxide (MnO_x) catalyst at room temperature [22]. Supported MnO_x is the most commonly used catalyst in OZCO of VOCs because of its superior ozone decomposition ability [23–26]. Nevertheless, the utilization of ozone in a conventional OZCO reaction is greatly depressed because HCHO is normally present at low concentrations indoors. This might lead to energy wasted on ozone production and cause secondary pollution owing to a continuous exhaust of incompletely decomposed ozone into the air.

To improve ozone utilization, effectively reduce energy costs, and minimize secondary pollution caused by undecomposed ozone during the HCHO removal process, in this work we used a cycled storage-OZCO approach to eliminate HCHO. The cycled HCHO storage-OZCO process was conducted over a supported MnO_x/Al_2O_3 catalyst at room temperature and included two stages, namely, a HCHO storage stage and an OZCO stage. In the storage stage, a low concentration of HCHO in the air was first adsorbed on the MnO_x/Al_2O_3 surface. Subsequently, at the OZCO stage, stored species, including formate and dioxymethylene (DOM), from HCHO adsorption were converted into CO_2 and H_2O by ozone oxidization [27]. The MnO_x/Al_2O_3 adsorption sites were regenerated to allow further storage in the next cycle. This storage-OZCO process offers two main advantages for overcoming the limitations encountered by conventional continuous OZCO methods. First, ozone is supplied only at the OZCO stage; thus, the consumption of ozone and associated energy costs are considerably reduced. Second, at the OZCO stage, a large amount of surface species, accumulated during the storage stage, can react with oxidative species from ozone decomposition effectively over a relatively short period. This effect not only facilitates an improvement of ozone utilization compared with the continuous OZCO reaction, but also considerably reduces pollution caused by undecomposed ozone. Therefore, we expect that cycled storage-OZCO processes could be used for indoor HCHO purification. To the best of our knowledge, the removal of low concentrations of HCHO using a cycled storage-OZCO process has not yet been reported.

2. Experimental

2.1. Catalyst preparation

In this work, γ-Al_2O_3 supported MnO_x catalysts were prepared by an incipient wetness impregnation method. To examine the effects of the manganese precursor, manganese(II) nitrate (mass fraction 50%, $Mn(NO_3)_2$) and manganese(II) acetate ($Mn(CH_3COO)_2$) were used as the precursors. The impregnated samples were first aged at room temperature for 15 h, and then dried at 110 °C for 6 h. The dried samples were then calcined at 500 °C for 4 h in air to obtain fresh MnO_x/Al_2O_3 catalysts.

2.2. Catalyst characterization

The phase composition of the MnO_x/Al_2O_3 catalysts was identified by X-ray diffraction (XRD) with use of a PANalytical Empyrean diffractometer with a Cu K_α radiation source. The XRD patterns were collected in the 2θ range of 20°–80° at a scanning rate of 5°/min with Cu K_α radiation ($\lambda = 0.154$ nm) at 40 kV and 40 mA. Brunauer-Emmett-Teller (BET) surface areas of the catalysts were measured by N_2 adsorption-desorption isotherms at −196 °C (Micromeritics ASAP 2020 V3.01, USA). Before the measurements, the samples were first pretreated at 350 °C for 10 h under vacuum. X-ray photoelectron spectroscopy (XPS; ESCALAB250 ThermoVG, USA) was performed with an Al K_α X-ray source (1486.6 eV), operated at 15 kV and 300 W, to examine the surface chemical states of the MnO_x/Al_2O_3 catalysts. The samples were first outgassed overnight under a vacuum of 10^{-5} Pa and then tested in the analytical chamber of the XPS spectrometer under 10^{-8} Pa. The binding energies were calibrated against the XPS spectra of the C 1*s* peak at 284.6 eV. Temperature programmed oxidation (TPO) experiments were performed over the catalysts after one HCHO storage-OZCO cycle. The used catalysts were first purged with a dry simulated air stream (20% O_2 balance N_2) at a flow rate of 250 mL/min at room temperature for 30 min before the TPO test. Subsequently, a temperature programed course was performed in simulated air (100 mL/min) from room temperature to 350 °C with a constant rate of 5 °C/min. The gas products were monitored online with a CO_x analyzer (S710, SICK/MAIHAK, Germany).

Diffuse reflectance infrared Fourier-transform (DRIFT) spectra of the MnO_x/Al_2O_3 catalysts during the cycled HCHO storage-OZCO process were recorded by an FT-IR spectrometer (Nicolet 6700, Thermo Fisher, USA) with an MCT detector operated at a resolution of 4 cm^{-1} from 4000 to 1000 cm^{-1}. Fresh MnO_x/Al_2O_3 samples were placed in a DRIFT cell (equipped with KBr windows) and pretreated with 200 mL/min Ar at 500 °C for 2 h and then cooled down to room temperature. Before the DRIFT measurements, the samples were further treated with 200 mL/min simulated air (containing 150 ppm O_3) for 1 h. The background reference was collected with a fresh MnO_x/Al_2O_3 sample at room temperature in simulated air (200 mL/min). Subsequently, two HCHO storage-OZCO cycles were conducted. At the storage stage, 200 mL/min of simulated air (containing 15 ppm HCHO) was flowed through the catalyst for 1 h. At the OZCO stage, 200 mL/min of simulated air (containing 150 ppm O_3) was used to oxidize the catalyst for 30 min.

2.3. Catalytic performance measurement for HCHO storage-OZCO process

Fig. 1 illustrates a schematic diagram of the experimental setup used in the cycled storage-OZCO process. The HCHO used in this work was produced by depolymerization of trioxymethylene vapor in a N_2-diluted gas stream. The depolymerization reaction was conducted at 160 °C over glass pellets coated with