Catalytic oxidization of indoor formaldehyde at room temperature — Effect of operation conditions

Zhiqiang Wang [a,1], Jingjing Pei [a,*], Jianshun Zhang [b,2]

[a] Tianjin University, School of Environmental Science and Engineering, Building 14, Room 240C, 92 Weijin Road, Naikai District, Tianjin 300072, China
[b] Syracuse University, Department of Mechanical and Aerospace Engineering, USA

ABSTRACT

Catalytic oxidization has been studied for elimination of formaldehyde, which is a common and toxic indoor pollutant. However, most of previous studies were conducted at temperature and concentration level much higher than typical room condition. The current paper is to determine the effectiveness of catalytic oxidization of formaldehyde at room condition. The performance of one noble metal catalyst (Pd/γ-Al_2O_3) and two transition metal oxide catalysts (Fe_2O_3–MnO_2 and CuO–MnO_2) were studied at room temperature (23–25 °C). The effect of concentration (0.5–5 ppm), relative humidity (20–80%) and air velocity (0.2–1.0 m/s) were studied with single-pass breakthrough method. The major conclusions are: (1) Under room temperature and much lower concentration levels than in previous studies, the noble metal catalyst also demonstrated significantly better removal performance than metal oxide, maintaining a constant efficiency with time; (2) For different concentration levels, the efficiency of Pd/γ-Al_2O_3 did not change significantly at concentrations below 5 ppm, while the efficiency increased as concentration decreased for Fe_2O_3–MnO_2; (3) the effect of relative humidity on the catalysts performance was not consistent for different type of catalysts; (4) Regarding the mass transfer mechanism, the importance of external mass transfer process was revealed by tests at different velocity for surface coated catalyst and dimensionless analysis, while both internal diffusion and external mass transfer are influential for homogeneously formed catalyst pellet. (5) The effect of multi-pollutants existence was also investigated, and it was found that the presence of other VOCs slightly decrease the performance of Pd/γ-Al_2O_3, but not Fe_2O_3–MnO_2.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Formaldehyde is one of the most common and concerned indoor gaseous pollutants. In indoor environment, it is normally emitted from wood products bonded with urea formaldehyde resins (e.g. gypsum wallboard, particle boards) and other household products. It is harmful to people's health, and is considered to be carcinogenic to humans [1]. While most of indoor volatile organic compounds (VOCs) can be effectively removed by porous sorbent media, the performance of physical adsorption for formaldehyde removal is not satisfactory. Some approaches that have been studied for formaldehyde removal includes chemisorption [2–5], photocatalytic oxidation (PCO) [6–9], thermal catalytic oxidization [10–12], plasma [13,14], botanical filtration [15–18], and biological filtration [19–21]. Among all these air cleaning technologies, catalytic oxidization appears to be an effective and promising approach for indoor formaldehyde removal. Investigated catalysts were mainly transition metal oxide and supported noble metal. Tang et al. observed 100% conversion of formaldehyde with platinum (Pt) promoted MnO_x-CeO_2 catalyst at room temperature [22]. At a lower concentration (280–500 ppb), Xu et al. observed a single pass efficiency of 35.4% at room temperature with Pt/MnO_x–CeO_2 catalyst [23]. With inexpensive manganese oxide deposited on particle filter, the experiment result from Lawrence Berkeley National Laboratory (LBNL) showed over 80% formaldehyde single pass efficiency at typical indoor concentration and velocity level [24]. However, long term test was not conducted, and the influence of concentration level, presence of other VOCs was not studied comprehensively.

The catalytic oxidization of VOCs can normally be described by Langmuir–Hinshelwood (L–H) mechanism, Eley–Rideal (E–R) mechanism, and Mars–van Krevelen (MvK) mechanism [25]. In

* Corresponding author. Tel.: +86 22 27403416 (office), 86 18622407076 (cell); fax: +86 22 27401561.
E-mail addresses: zqwang@tju.edu.cn (Z. Wang), jpei@tju.edu.cn (J. Pei), jszhang@syr.edu (J. Zhang).
[1] Tel.: +86 13512830852 (cell).
[2] 263 Link Hall, Syracuse University, Syracuse, NY 13244, USA. Tel.: +1 315 443 1366; fax: +1 315 443 9099.

most cases, the catalytic oxidization by noble metal catalyst follows MvK mechanism [24,26–28]. The catalytic process is initiated with the oxidization of adsorbed formaldehyde molecule ($\cdot$CHO) by active oxygen species (O^{*-}), which generates formate ($HCOO^{-}$); then the C–H bond of the formate is further attacked by the oxygen species (O^{*-}), and finally form CO_2 and H_2O [29–31].

In a review of catalytic oxidization of formaldehyde for indoor air cleaning application [25], the effect of operation conditions on the performance of catalysts was summarized. Most of the studies on catalytic oxidization of formaldehyde were conducted at temperature above 100 °C, at which complete oxidization of formaldehyde turns possible [10,32]. There were limited studies showed effectiveness of catalysts at room temperature [11,31,33–35]. Moreover, formaldehyde concentrations in previous studies were normally in the range of 100–1000 ppm, some were even higher at thousands of ppm. This is much higher than that experienced in indoor environment, which is in sub-ppm level. There was one study [10] investigated the effect of concentration (100–400 mg/ m^3) on Pt/TiO2 catalyst, and found higher formaldehyde conversion efficiency at lower concentration. Research on the effect of relative humidity on catalyst was also limited.

In general, the study on how the concentration level, relative humidity and face velocity affect the performance of catalyst for formaldehyde removal was limited, especially under typical room condition. This study focused on the performance evaluation of several commercially available catalysts for indoor formaldehyde removal under room temperature. The effect of relative humidity, concentration and velocity was studied, in order to identify the optimum operation condition that can be reached in typical HVAC system and improve the understanding of the removal mechanisms as influenced by catalyst properties and operation conditions.

2. Material and method

2.1. Catalysts and their characterization

Three commercially available catalysts were studied in this study. They are Pd/γ-Al2O3 (from Johnson Matthey), Fe2O3–MnO2 (from Süd-Chieme), and CuO–MnO2 (from Carus). The Pd catalyst is coated on the surface of 2–4 mm diameter γ-Al2O3 sphere. The Fe2O3–MnO2 catalyst is composite of 50–65 wt% Fe2O3 and 25–50 wt% MnO2 as provided by the supplier. The percentage composition of CuO–MnO2 is not available from the material data sheet.

The scanning electron microscope (SEM) images of these catalysts were taken. Nano golden particle was coated on the surface of the sample before analysis. The BET surface area, total pore volume, and pore size distributions were analyzed by N_2 adsorption using Micromeritics ASAP 2020. The pore size distribution is generated with Barrett–Jovner–Halenda (BJH) adsorption model.

2.2. Performance test method

The formaldehyde removal performance of the catalyst was evaluated with a single pass test system. The formaldehyde concentration was measured by an online photo-acoustic multi-gas monitor (Lumasense INNOVA 1312), and the detection limit is 0.046 ppm. The detailed setup description and test procedure can be found in the previous study [2]. The catalyst was packed in a stainless steel column for test. The flow rate through the packed column was 0.63 LPM for a face velocity of 0.54 m/s, with corresponding GHSV as 1.25×10^5 h^{-1}. For each test, the sample was preconditioned with desired RH airflow for 3 h to reach equilibrium with water vapor before exposure to formaldehyde-polluted air. All tests were conducted at room temperature (23–25 °C). Each test lasted for a time period that quasi-steady state was reached, means

the change of downstream concentration over the last 1 h was less than 5%.

The effect of multi-VOCs existence on the performance of the catalytic oxidation of formaldehyde was investigated with a "pull-down" test method using a closed recirculation system. VOC mixture was injected into the system by air flow through solid para-formaldehyde with/without other liquid VOC mixture in a temperature controlled oven. The catalyst was packed in a 5 mm I.D. stainless steel tube, which is connected in the recirculation system. A recirculation pump was used for passing air through the catalyst. The system concentration was monitored continuously by Proton Transfer Reaction-Mass Spectrometry (PTR-MS, Ionicon Analytik, Austria) and experienced exponential decay during the test. Tests were conducted with formaldehyde only and formaldehyde with 3 other VOCs (toluene, 1-butanol and decane).

2.3. Data analysis

In the single pass test, the residence time was calculated by the depth of the packed catalyst divided by the velocity. The removal capacity or single pass efficiency was calculated as performance evaluation parameter. The capacity is a weight percentage of removed formaldehyde per unit weight of catalyst at certain breakthrough point (i.e. 80% BT means downstream concentration reaches 80% of upstream concentration). The single pass efficiency was calculated by the difference between upstream and downstream concentration.

In the recirculation pull-down test investigating the effect of multi-VOC effect, the average single pass efficiency for each test was calculated with a mass balance model as:

$$\eta = \frac{(N - N_0) \cdot V}{Q} \tag{1}$$

The average VOC removal rate during the first hour of the test was also calculated as:

$$R = \frac{(c - c_0) \cdot V}{T} \tag{2}$$

where N is the concentration decay rate (h^{-1}) of each VOC with media, N_0 is the decay rate (h^{-1}) of each VOC without media, Q is the air flow rate through the media column, c is the chamber concentration with media at time T; c_0 is the chamber concentration without media at time T; T is the time of averaging period (1 h if the removal rate is calculated for the first 1 h average), V is the volume of the system (approximately the volume of the mixing chamber).

3. Results and discussions

3.1. Catalyst characterization

The SEM image of the sample is shown in Fig. 1. All the three catalysts are porous, and there is no significant porosity difference presented. The physical properties, obtained BET surface area and pore properties are listed in Table 1. Those catalysts generally have a BET surface area in the range of 100–300 m^2/g, which is much less than that for sorbent material. Due to the high vapor pressure of formaldehyde, it cannot be easily adsorbed even by sorbent with >1000 m^2/g surface area. Therefore the adsorption effect by the catalyst is assumed to be negligible compared with catalytic reaction effect.

Fig. 2 shows the pore size distribution of the catalysts. Both the average pore diameter and the pore distribution chart show that the Pd catalyst has smaller pores than the other two metal oxide catalysts, but all in the order of 10 nm.