Chemosphere 78 (2010) 1110–1115

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Low-temperature catalytic oxidation of aldehyde mixtures using wood fly ash: Kinetics, mechanism, and effect of ozone

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ARTICLE INFO

Article history:
Received 10 June 2009
Received in revised form 14 December 2009
Accepted 15 December 2009
Available online 12 January 2010

Keywords:
Rendering
Odors
VOCs
Catalyst
Low-temperature

ABSTRACT

Poultry rendering emissions contain volatile organic compounds (VOCs) that are nuisance, odorous, and smog and particulate matter precursors. Present treatment options, such as wet scrubbers, do not eliminate a significant fraction of the VOCs emitted including, 2-methylbutanal (2-MB), 3-methylbutanal, and hexanal. This research investigated the low-temperature (25–160 °C) catalytic oxidation of 2-MB and hexanal vapors in a differential, plug flow reactor using wood fly ash (WFA) as a catalyst and oxygen and ozone as oxidants. The oxidation rates of 2-MB and hexanal ranged between 3.0 and 3.5×10^{-9} mol g^{-1} s^{-1} at 25 °C and the activation energies were 2.2 and 1.9 kcal mol^{-1}, respectively. The catalytic activity of WFA was comparable to other commercially available metal and metal oxide catalysts. We theorize that WFA catalyzed a free radical reaction in which 2-butanone and CO_2 were formed as end products of 2-MB oxidation, while CO_2, pentanal, and butanal were formed as end products of hexanal oxidation. When tested as a binary mixture at 25 and 160 °C, no inhibition was observed. Additionally, when ozone was tested as an oxidant at 160 °C, 100% removal was achieved within a 2-s reaction time. These results may be used to design catalytic oxidation processes for VOC removal at poultry rendering facilities and potentially replace energy and water intensive air pollution treatment technologies currently in use.

1. Introduction

Many industrial operations generate aldehydes as air pollutants (Baumann et al., 2000; Fullana et al., 2004). For example, 3-methylbutanal (3-MB), 2-methylbutanal (2-MB), and hexanal are generated in poultry rendering operations when animal by-products are processed (Kastner and Das, 2002). The aldehydes are odorous (Brewer et al., 1999), and contribute to atmospheric ozone and particulate matter formation. Typically, chemical wet scrubbers are used to treat aldehydes and other volatile organic compounds (VOCs) by oxidizing them with chemical oxidants, such as ClO_2 and/or O_3 (Kastner and Das, 2005). However, on-site analysis of the wet scrubbers indicated low removal efficiencies when treating aldehydes (typically <50%), due to lack of reactivity between the aldehydes and ClO_2 (Kastner et al., 2003).

Traditional treatment technologies such as adsorption, incineration, and biological filtration have limitations (Tsou et al., 2003). Adsorption only transfers and concentrates the VOCs from a gas phase onto a solid phase and needs further treatment for complete removal (Everaert and Baeyens, 2004). Incineration requires combustion of the VOCs at high temperatures (1000–1200 °C) using natural gas as a fuel source, is costly and contributes to greenhouse gas production (Gervasini and Ragaini, 2000). Biological filtration systems need long residence times (30–60 s) and thus have large footprints. Hence, an effective alternative technology is needed to treat the aldehyde fraction from rendering emissions.

Catalytic oxidation is a promising alternative technology to treat VOCs (Gervasini and Ragaini, 2000). The process involves reaction between VOCs and an oxidant, aided by a catalyst. Catalysts lower oxidation temperatures by providing alternate routes to end products, whose activation energies are less than that of non-catalytic reactions and typically increase reaction rates. Lowering the reaction temperature lowers treatment costs and reduces the production of greenhouse gases. Expensive metals (e.g., gold, platinum) and metal oxides (e.g., nickel oxide, ruthenium, etc.) have been tested as catalysts with a high degree of success. However, research has been limited on the development of catalysts from inexpensive materials, especially solid wastes.

Many solid waste sources contain metals or metal oxides of sufficient surface area to be reused as catalysts (Klose et al., 2000). Wood fly ash (WFA), as an example, is produced in large amounts in the USA (5.5 Mt y^{-1}), with a majority land filled (Demeyer et al., 2001). Analysis of WFA revealed crystalline phases of metal oxides (magnetite and hematite) and activated carbon in its structure.

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doi:10.1016/j.chemosphere.2009.12.033

WFA catalytically oxidizes H_2S using O_2, and oxidizes volatile organic sulfur compounds and propanal, in the presence of ozone (Kastner et al., 2005, 2008).

Additionally, WFA catalytically oxidizes 3-MB at room temperature via a free radical mechanism (Kolar et al., 2007). However, a complete carbon balance on the reactions was not performed and it is unclear if complete oxidation occurred. Additionally, this work focused on single aldehyde (3-MB) oxidation, when in reality, rendering emissions consist of aldehyde mixtures, making it difficult to predict the catalytic performance based on a single compound. Hence, it is critical to evaluate WFA as a low-cost catalyst to treat aldehyde mixtures normally encountered in rendering emissions. The objectives of this study were to evaluate WFA as a low-cost catalyst for treating a binary aldehyde mixture at low-temperatures (25–160 °C), determine the kinetics of oxidation reactions and activation parameters, identify and quantify the oxidation products, perform a complete carbon balance, and determine the effect of ozone on the oxidation processes.

2. Experimental

2-MB and hexanal (95%, Sigma–Aldrich) were used as representative aldehydes in this study because of their consistent occurrence in poultry rendering emissions (Kastner and Das, 2002).

2.1. WFA characterization

The WFA used in this study was obtained from a paper mill. The physical and chemical properties were determined previously (Kolar et al., 2007). In this study a scanning electron microscope (SEM) was used to image the WFA and energy dispersive spectroscopy (EDS) used to determine the elemental composition of the ash particle surface (see Supplemental material (SM). SM 1.1).

2.2. Description of experimental setup and analytical methods

All gas/solid phase reactions were carried out in a 30-cm long, 2.5-cm diameter (ID) continuous flow, differential packed-bed reactor system, as described previously (Kastner et al., 2005 and SM 1.2–1.3). A combination of gas chromatographs equipped with mass selective and flame ionization detectors were used for analysis on the reactants and end products.

2.3. General experimental procedures

We determined the kinetics of individual aldehydes, kinetics of a binary mixture, the effect of temperature, and the effect of 1500 ppmv ozone on oxidation of 2-MB and hexanal. The total flow for the entire study was between 2.0 and 5.0 L min^{-1} (GHSV = 0.0011–0.0055 h^{-1}). For studies in which air was used as an oxidant, the ratio of oxygen to substrate ranged between 525:1 and 10 000:1. Similarly for experiments with ozone as an oxidant the ratio ranged between 3.75:1 and 5:1. Detailed experimental procedures are outlined in the SM 1.4–1.6.

3. Results and discussion

3.1. Effect of oxygen and evidence of catalytic activity

Preliminary experiments were conducted to determine the effect of oxygen on catalytic oxidation of aldehydes. When ultra high pure helium (5 L min^{-1}, 25 °C) was used as the carrier gas (no oxygen present), fractional removal of 2-MB was limited to 2% which was probably due to sampling error. However, when pure oxygen was added to the system (helium:oxygen = 4:1; total flow: 5 L min^{-1}, 25 °C), the fractional removal increased from 2% to 10% indicating that the removal was due to the catalytic reaction between oxygen and 2-MB in the presence of WFA (data not shown). This observation was in agreement with our earlier work with 3-MB where the presence of oxygen increased the fractional removal from 2% to 20% (Kolar et al., 2007).

3.2. Kinetics of individual aldehydes

The overall rate of 2-MB and hexanal oxidation was found to increase with an increase in 2-MB or hexanal concentration (0–120 ppmv, 25 °C, Fig. SM-1) and both the Power Law and Mars van Krevelen models (O_2 in excess) were used to determine kinetic parameters (Fig. SM-2). For the power law model, the order of the reaction was 1.13 and the rate constant 6.2×10^{-3} $mol^{-0.13}$ $L^{1.13}$ g^{-1} s^{-1} for 2-MB and 0.83 and 1×10^{-4} $mol^{0.17}$ $L^{0.83}$ g^{-1} s^{-1} for hexanal respectively. When the Mars van Krevelen model was fit to the data, the rate constants were 9.6×10^{-4} L g^{-1} s^{-1} for 2-MB and 1.4×10^{-3} L g^{-1} s^{-1} for hexanal.

The oxidation rates of 2-MB and hexanal were similar to that previously reported for 3-MB (Kolar et al., 2007). However, the rates in this work were generally lower than other published studies on aldehyde oxidation using metal supported catalysts (Table 1). For example, Liakopoulos et al. (2001) reported oxidation rates of $13–14 \times 10^{-8}$ mol g^{-1} s^{-1} when acetaldehyde (360 and 510 ppmv) was oxidized at 205 °C using Pt/Rh catalysts and excess oxygen. Similarly, formaldehyde oxidation rates using manganese and cerium oxide catalysts at 50–100 °C were reported as 5×10^{-8} mol g^{-1} s^{-1} (Tang et al., 2006). Our rates were also lower than other VOCs studied. For example, reaction rates ranged between $1–18 \times 10^{-8}$ mol g^{-1} s^{-1} for *n*-hexane (164–221 °C) and $1–5.5 \times 10^{-8}$ mol g^{-1} s^{-1} for benzene (140–170 °C), when catalytic oxidation of n-hexane (201–566 ppmv) and benzene (9–525 ppmv) using air over 0.1% Pt, 3% Ni/γ-Al_2O_3 catalyst was studied (Gangwal et al., 1998).

Table 1
Comparison of aldehyde oxidation rates with various catalysts using oxygen. Reaction rates were estimated from the literature, where noted (RH = 0% for studies in the literature).

VOC	Concentration (ppmv)	Catalyst	Temp (K)	End products	Rate (mol g^{-1} s^{-1})
Propanal[a]	20 000	Mn_3O_4	560	Acetaldehyde, CO_2	11×10^{-7}
Formaldehyde[b]	580	Oxides of Mn–Ce	333–373	ND	50×10^{-9}
3-MB[c]	45–68	Wood fly ash	298–433	Acetone	$4–10 \times 10^{-9}$
2-MB[d]	20–120	Wood fly ash	298–433	2-butanone	$3–5 \times 10^{-9}$
Hexanal[d]	20–120	Wood fly ash	298–433	Pentanal, butanal	$3–11 \times 10^{-9}$
Acetaldehyde[e]	360–510	Pt/Rh	498	CO_2	$110–140 \times 10^{-9}$

ND: Not determined.
[a] Baldi et al. (1998).
[b] Martyanov et al. (2005).
[c] Kolar et al. (2007).
[d] This work.
[e] Liakopoulos et al. (2001).