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Catalytic oxidation for elimination of methyl bromide fumigation emissions using ceria-based catalysts

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A B S T R A C T

Methyl bromide (CH_3Br, MB) is an effective chemosterilant in quarantine and pre-shipment (QPS) chamber fumigation applications. Efficient methods to destroy or capture and reuse spent MB in QPS operations are required in view of the recognized ozone depleting potential of MB. Oxidation of 34,000 ppmv MB in simulated QPS airstreams was examined over catalysts composed of Pt, Pd, Fe_2O_3, CuO, or PbO nanoparticles on oxide (Al_2O_3, SiO_2, and TiO_2) or mixed-oxide ($CeO_2–Al_2O_3$, $CeO_2–SiO_2$, and $CeO_2–TiO_2$) supports, and by self-assembled core–shell catalysts (Pd@SiO_2 and Pd@10%$CeO_2–Al_2O_3$). The most effective support by far was ceria. The effect of noble metal doping was modest; Pt was more active than Pd in $CeO_2–Al_2O_3$ based catalysts, while Pd was more active than Pt in TiO_2 based catalysts. The most effective catalyst tested was 1%Pt/30%$CeO_2–Al_2O_3$, with 100%CeO_2 being only slightly less effective. Using 1%Pt/30%$CeO_2–Al_2O_3$, MB was completely oxidized at 400 °C, independent of airstream humidification, to give HBr as the initial product, which was subsequently oxidized to Br_2 by a Deacon-type reaction. The selectivity for Br_2 in MB decomposition increased with temperature, maximizing at ~90% at ~350 °C, and was slightly less favored in a humidified air stream. Bromide builds up on the catalyst at temperatures below 300 °C, but burns off as the temperature increases. Catalytic oxidation by ceria-based catalysts appears to be a promising approach for eliminating MB from QPS fumigation emissions.

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1. Introduction

Methyl bromide (MB) has been widely used historically as a soil fumigant and chemosterilant for durable and fresh commodities in trade channels [1]. In 1992 MB was listed as an ozone depleting substance under the Montreal Protocol. Its use was to be phased out by 2005 in the United States and other developed countries [2], and by 2015 in developing countries [3]. However, the Montreal Protocol allows critical use exemption (CUE) [4] or quarantine and pre-shipment (QPS) exemption [5] in cases where feasible technical or economical replacements are lacking. As a result, except for a complete ban of MB use within the European Union (effective March 18, 2010) [6], MB is still in use in most countries [7] under the auspices of CUE or QPS exemptions. In typical QPS fumigations, the commodity is treated in a chamber and the spent MB vapors are then vented to the atmosphere. Development of methods to destroy or capture and reuse spent MB is urgently needed to eliminate MB emissions for environmental and health reasons, as well as to preserve the current QPS exemption for MB.

Several approaches for trapping or degrading MB vapors have been tested, but few of them are practical for dealing with chamber fumigation situations. MB emissions from soil fumigation have been transformed in a reactive layer of ammonium thiosulfate between two layers of plastic film [8], or by injecting NH_4OH beneath an impermeable film [9]. Methyl bromide undergoes nucleophilic attack by those reagents. Chamber emissions have been captured by activated carbon [10–12]. Leech et al. [10] demonstrated that activated carbon could adsorb up to 10% by weight of MB in a vent stream initially containing 16,000 parts per million by volume (ppmv) MB (average concentration, 3800 ppmv). Later, Snyder and Leesch combined activated carbon adsorption with electrothermal regeneration [11]. Gan and Yates [12] captured and decomposed MB in a slurry of activated carbon in sodium thiosulfate solution; decomposition required from 0.5 to 9 h at 20 °C. The addition of triethylene diamine (TEDA) to coconut shell activated carbon was reported to increase MB breakthrough time and result in methylation of TEDA by MB, but the overall removal capability of MB was adversely affected by humidity [13]. Despite the limited successes of these methods, none of them has been able to reach widespread use. This may be due to practical or economic obstacles, such as slow reaction, adsorptive competition by water vapor, or additional costs to dispose or regenerate the adsorbent. With these considerations, further research on

novel methods to destroy or capture and reuse spent MB is warranted.

The removal of hazardous volatile organic compounds (VOCs) and gases such as CO, SO_x and NO_x from exhaust streams is required in automobile operation and many industrial processes. One of the most effective techniques is catalytic oxidation, in which a solid catalyst is employed to lower the temperature of thermal oxidation, often by several hundred degrees [14,15]. Three main types of combustion catalysts for VOCs have been studied: supported noble metals [16,17], transition metal oxides [18,19], and zeolites [20,21]. Halogenated VOCs (HVOCs) have received relatively little attention compared to non-halogenated VOCs. Catalytic oxidation seems a promising alternative for removal of MB because it uses "free" reagents (air) and is expected to convert MB instantly and completely to inorganic products.

Ceria (CeO_2) has been widely used as a promoter when added to high surface area supports such as Al_2O_3 and SiO_2. Ceria is a central component of catalysts used in the treatment of automobile exhausts, removal of SO_x and NO_x from flue gases, and selective oxidation reactions [22]. Relative to other oxide supports, ceria improves catalyst performance by inhibiting sintering of noble elements [23], promoting dispersion of noble metals on the support [24], facilitating noble metal reduction and oxidation [22], increasing thermal stability of co-components [25], and increasing overall catalytic efficiency in mixtures with other oxide supports [26–29]. Moreover, ceria has higher intrinsic catalytic activity than other supports. A key property of ceria is its ability to form a continuum of oxygen-deficient, nonstoichiometric oxides (CeO_{2-x}; $0 < x \leq 0.5$), while retaining its (fluorite) crystal structure (Eq. (1)),

$$O_{lat} + 2Ce_{lat}^{IV} \leftrightharpoons \square + 2Ce_{lat}^{III} + \frac{1}{2}O_2 \tag{1}$$
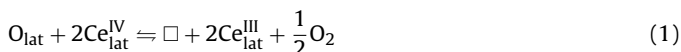
where O_{lat} is lattice oxygen, Ce_{lat}^{IV} is normal lattice cerium, $\square$ is a lattice oxygen vacancy and Ce_{lat}^{III} is the reduced form of lattice Ce. This reaction is reversible [22], so that ceria acts as an oxygen storage material in catalyzed oxidations [30]. Noble metals (Pt, Pd or Rh) promote reduction of Ce_{lat}^{IV} to Ce_{lat}^{III} and increase oxygen storage capacity [31,32]. Addition of ceria to (Pt, Pd, or Rh)/Al_2O_3 appears to decrease the activation energy for oxidation of CO and HCs [32]. Vacancies and "active" oxygen involved in the pathway of reaction 1 are believed to play roles in the oxidation of VOCs and other gases [22,30].

Oxidation of hydrocarbons (HCs) over ceria-based catalysts is thought to proceed by the Mars-van Krevelen redox cycle, in which the first step is hydrogen abstraction by a coordinatively unsaturated active surface lattice oxygen, O_{lat}^*, giving CO_2 and H_2O, which desorb, exposing vacancies that are replenished by gas-phase dioxygen [29,33]:

$$O_{lat} \rightarrow O_{lat}^* \tag{2}$$

$$HC + \beta O_{lat}^* \rightarrow P + \beta\square \tag{3}$$

$$\square + \frac{1}{2}O_2 \rightarrow O_{lat} \tag{4}$$

where β is the stoichiometric ratio forming product P. The combustion of methane over Pd oxide-based catalysts has been studied in great detail and likely proceeds similarly [34]. The participation of lattice oxygen species in HCl oxidation on metal oxides can also be supported experimentally by temporal-analysis-of-products technique [35]. Whether step 3 or some other step is central to HVOC oxidation has not been established. In some cases, Lewis acid–base chemistry is likely involved, as chloroethene is an intermediate of 1,2-dichloroethane oxidation catalyzed by ceria and ceria–zirconia mixed oxides [36].

While the high activity of CeO_2 catalysts toward other VOCs and HVOCs is known, there are no reports on the combustion of MB using CeO_2-based catalysts. In fact, the only report to our knowledge on catalyzed thermal oxidation of MB is one by Windaw and Zhang [17], who published the ignition curves of MB over Pt/Al_2O_3 and Pt/TiO_2 in the course of addressing the competitive effect of MB on toluene oxidation. One objective of our study was to screen CeO_2-based and other supported oxide catalysts for activity toward MB in air streams simulating vent streams from QPS chamber fumigations. A second was to shed some light on the reaction mechanism using the most active catalyst found.

2. Experimental

2.1. Catalyst preparation

Catalysts prepared by wet impregnation. Catalysts of Pt, Pd, Fe_2O_3, CuO, and PbO on oxide supports, Al_2O_3, SiO_2, and TiO_2, and mixed oxide supports, CeO_2–Al_2O_3, CeO_2–SiO_2, and CeO_2–TiO_2, were prepared via wet impregnation [29,37]. Hydrogen hexachloroplatinate ($H_2Cl_6Pt\cdot6H_2O$, Acros Organics, 99.90%), potassium tetrachloropalladate (K_2PdCl_4, Acros Organics, Pd $\geq$ 32%), ferric nitrate ($Fe(NO_3)_3\cdot9H_2O$, Mallinckrodt Chemical Works, 99%), copper nitrate ($Cu(NO_3)_2\cdot3H_2O$, Mallinckrodt Chemical Works, 99.9%), lead nitrate ($Pb(NO_3)_2$, Fisher Scientific, 99.95%), and cerium nitrate ($Ce(NO_3)_3\cdot6H_2O$, Acros Organics, 99.5%) were used as metal precursors, while Al_2O_3 (Fisher Scientific), TiO_2 (Sigma–Aldrich, $\geq$99%), SiO_2 (Spectrum Chemical Manufacturing Corp.), and CeO_2 (Acros Organics, 99.9%) were used as supports. The mixed oxide supports were prepared by adding Al_2O_3, SiO_2, or TiO_2 to aqueous solutions (100 mL) of cerium nitrate and mixing for 3 h. The product was dried at 110 °C for 24 h and then calcined in air at 500 °C for 5 h. Noble metal (1% Pt or Pd) or metal oxide dopants (5% Fe_2O_3, CuO, and PbO) were incorporated into the prepared mixed oxides (CeO_2–Al_2O_3, CeO_2–SiO_2, and CeO_2–TiO_2) or commercial oxides (Al_2O_3 and TiO_2) by the same mixing, drying, and calcination techniques. Weight percent was used unless specified.

Core–shell catalysts. This group includes Pd@SiO_2 and Pd@10%CeO_2–Al_2O_3. They were prepared in an identical manner as reported by Forman et al. [38] and Cargnello et al. [39], respectively. For preparing Pd@SiO_2, a mixture of tetraethyl orthosilicate and n-octadecyl trimethoxysilane was employed as the SiO_2 precursor, and hydrazine was used as the reducing agent. Pd@SiO_2 was precipitated, centrifuged and washed in ethanol, followed by drying and then calcining at 550 °C in air for 6 h. The Pd@10%CeO_2–Al_2O_3 was prepared by adding Al_2O_3 to synthesized Pd@CeO_2 which was prepared by exploiting the self-assembly between 11-mercaptoundecanoic acid-functionalized Pd nanoparticles and cerium decyloxide. After recovery from THF, the Pd@10%CeO_2–Al_2O_3 was dried and calcined at 500 °C for 5 h.

2.2. Catalyst characterization

Surface area was determined by gas adsorption on an Autosorb-1 gas analyzer (Quantachrome Instrument Corp., Boynton Beach, FL) after outgassing at 200 °C, by application of the Brunauer–Emmett–Teller (BET) equation to an 11-point adsorption isotherm of N_2 at 77 K in the region 0.05–0.3 relative pressure. Metal loading was analyzed using Inductively Coupled Plasma Optical Emission Spectrometry by Galbraith Laboratories, Knoxville, TN. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8Focus diffractometer using a Ni-filtered Cu Kα radiation ($k = 0.154061$ nm), and operating at 40 kV and 40 mA. Diffraction data were collected between 20° and 80° (2θ) with a resolution of 0.05° (2θ). Structural morphology was investigated