



An investigation on the structure and catalytic activity of cryptomelane-type manganese oxide materials prepared by different synthesis routes



Catherine Almquist^{a,*}, Mark Krekeler^b, Lulu Jiang^a

^a Chemical and Paper Engineering Department, Miami University, Oxford, OH 45056, United States

^b Geology Department, Miami University, Hamilton, OH 45011, United States

HIGHLIGHTS

- Cryptomelane was prepared by three different methods: reflux, sol–gel, and milling.
- Post-consumer alkaline battery waste was used to prepare a milled sample.
- >95% Degradation of ethanol (inlet conc. <500 ppm) at 200 °C for all samples.
- The activation energies for ethanol oxidation over cryptomelane was ~65 kJ/mole.
- The catalyst activity of cryptomelane samples was stable for up to 8 days.

ARTICLE INFO

Article history:

Received 20 January 2014

Received in revised form 23 April 2014

Accepted 26 April 2014

Available online 9 May 2014

Keywords:

Cryptomelane

Alkaline battery waste

VOC catalyst

ABSTRACT

Cryptomelane is an octahedral molecular sieve with a 2×2 tunnel structure (OMS-2) and a stoichiometric formula of approximately $\text{KMn}_8\text{O}_{16}$. Cryptomelane OMS-2 is gaining increasing attention in a range of applications, including catalysis. However, the impacts of synthesis methods on catalytic performance are still not well understood. Cryptomelane OMS-2 was prepared in this study by three methods: (1) a sol–gel method, (2) a reflux method, and (3) a milling method. The physical and chemical characteristics of these materials were investigated, and the catalytic performances of these materials were compared for the gas phase oxidation of ethanol. A novel aspect of this study is that cryptomelane was prepared by the milling method using post-consumer alkaline battery waste, and this novel cryptomelane material was compared with others prepared from commercially-available precursors and published laboratory methods.

Cryptomelane prepared from battery waste via the milling method has a low surface area ($4 \text{ m}^2/\text{g}$) and a lower catalytic activity than cryptomelane samples prepared in this study with purchased chemicals. However, all cryptomelane samples used in this study, including the samples prepared from battery waste, could oxidize ethanol vapors at inlet concentrations ≤ 500 ppm by greater than 95% at 200 °C. The catalytic activities of all cryptomelane samples studied were stable for up to 8 days at a reaction temperature of 175 °C at an inlet ethanol concentration of 400 ppm. The implication of this study is that post-consumer alkaline batteries may be used as a raw material for volatile organic carbon oxidation catalysts.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Cryptomelane is a manganese oxide octahedral molecular sieve (OMS) with a 2×2 tunnel structure and a stoichiometric formula of approximately $\text{KMn}_8\text{O}_{16}$. It has been investigated as a useful and active catalyst in several types of reactions in both

liquid and gas phases [1]. For example, cryptomelane was studied as a liquid-phase catalyst for selective oxidation reactions [2–10] and as a photocatalyst for degradation of contaminants in water [11]. It has been studied as a gas phase oxidation catalyst for the oxidation of carbon monoxide (CO) [12–17] as well as for the oxidation of volatile organic carbon (VOC) compounds, such as formaldehyde [18–23], ethyl acetate [24–29], ethanol [30–35] and other oxygenates [36,37], and aromatics [38–41], among others.

* Corresponding author. Tel.: +1 513 529 0767.

E-mail address: almquic@miamioh.edu (C. Almquist).

The activity of the catalyst has been reported to be a result of the mixed valence state of the manganese (Mn) and the mobility of the lattice oxygen in the cryptomelane surface structure [1,3–5,29,34,35,37]. In a review by Suib [1], it is stated that mixed valence is important in electron transfer, energy transfer, and redox catalysis and that oxygen vacancies are related to potential catalytic activity [1]. Therefore, the average oxidation state (AOS) of cryptomelane is important in characterizing the redox properties of cryptomelane, as some researchers have correlated AOS or redox properties with catalytic activity [1,19,31,33,34,37,38]. Other properties that impact catalytic activity have been found to include surface area [3,19,21] acidity [6,15], hydrophobicity [15,38,40], and morphology [16,19–22,33,38], among others.

The kinetic model most often proposed for the catalytic oxidation of organics on cryptomelane is the Mars-Van Krevelen mechanism [4,12,37,38]. There are two key steps in this mechanism: (1) lattice oxygen at the surface of the catalyst reacts with adsorbed organic compounds, which reduces manganese in cryptomelane from Mn^{4+} to Mn^{2+} and creates an oxygen vacancy in the catalyst, and (2) gas-phase oxygen replenishes the oxygen vacancy and oxidizes the reduced catalyst. According to a discussion by Makwana et al. [4], when the catalysis system is at steady-state, the rate at which the adsorbed organic compounds are oxidized by lattice oxygen equals the rate at which gas-phase oxygen replenishes the resulting oxygen vacancy. Under conditions of steady-state and excess oxygen in the system, the initial rate at which the organic compounds are oxidized over cryptomelane takes the form [4] depicted in Eq. (1):

$$-\frac{d[R]}{dt} = \frac{a[R]}{b + c[R]} \quad (1)$$

where [R] represents the concentration of organic substrate and a , b , and c are model parameters.

Researchers have doped cryptomelane in an effort to enhance its catalytic activity [12,14,23,29,37,38]. Enhanced catalytic activity as a result of adding a dopant to cryptomelane has been attributed to enhanced oxygen mobility, changes in average oxidation state, and changes in the reducibility of Mn at the surface of cryptomelane [13,37]. However, the dopant does not necessarily change the morphology of the cryptomelane. For example, Hernandez et al. (2010) doped cryptomelane with copper (Cu), cobalt (Co), nickel (Ni), and zinc (Zn) and found that the dopants do not have any noticeable effect on the structural or textural properties of cryptomelane [13]. However, the activity for CO oxidation was enhanced with Cu and Co, whereas very little change in activity was observed with Ni and Zn dopants [13].

This study focuses on the preparation, characterization and evaluation of cryptomelane and its activity for the catalytic oxidation of ethanol. Ethanol was selected because of its importance as an additive to gasoline and as a renewable fuel. In fact, the final EPA Renewable Fuel Standard targets 6 million gallons of cellulosic biofuels for 2013 [42], of which ethanol is a key component. The manufacture, distribution, and use of ethanol will generate ethanol emissions, which must be treated in pollution control operations. Catalytic oxidation utilizing volatile organic compound (VOC) catalysts is one method of controlling such emissions, and in this study, cryptomelane prepared by different synthesis methods is investigated as a VOC catalyst.

The motivation for this research was to assess whether cryptomelane prepared from post-consumer alkaline battery waste could be used as a VOC oxidation catalyst. This is the novel aspect of this study; the precursor to one of the cryptomelane materials prepared here is post-consumer alkaline battery waste, which contains zinc, manganese dioxide, and potassium hydroxide. It is estimated that nearly three billion of these batteries are purchased

and thrown away each year, amounting to nearly 100,000 tons of battery waste [43]. This waste typically ends up in landfills, where the metals in the batteries have potential to leach into the environment. Therefore, finding a use for this waste stream would have both economic and environmental benefits to battery manufacturers and users.

The recovered Mn-oxide and potassium hydroxide components from the batteries contains zinc, and so the resulting cryptomelane prepared from the battery waste also has zinc in it. What impacts will the zinc have on the catalytic activity of the cryptomelane?

The four key objectives of the study are to (1) assess the impact of synthesis method on the chemical and physical properties of cryptomelane and its catalytic activity for ethanol oxidation; (2) assess the impact of calcination temperature on the chemical and physical properties of cryptomelane and its catalytic activity, (3) assess the impact of zinc on cryptomelane's physical and chemical properties and on its catalytic activity for the gas-phase oxidation of ethanol, since alkaline battery waste contains zinc, and (4) compare the catalytic activity of cryptomelane made from battery waste with those synthesized with purchased chemicals. These objectives are supported by Prieto et al. (2003) who state that small changes in synthesis parameters can lead to materials with different catalytic properties [44].

2. Experimental methods

2.1. Cryptomelane synthesis

The cryptomelane was prepared in this study using three methods: (1) a sol-gel method, (2) a reflux method, and (3) a milling method. Each of these methods is described in more detail below.

2.1.1. Sol-gel method

The sol-gel method used here was described by Ching and Roark [45]. Briefly, a 100 mM solution of potassium permanganate ($KMnO_4$) was prepared. Fumaric acid ($C_4H_4O_4$) was added to the solution at a molar ratio of 3:1 $KMnO_4/C_4H_4O_4$. After adding the two chemicals into the deionized water, the mixture forms a brownish flocculent gel. The gel is then filtered, washed, dried, and calcined in air for 2 h. Finally the black cryptomelane is washed again with acidic water and then deionized water.

The sol-gel catalysts were used to investigate the role of calcination temperature on the properties and catalytic activity of cryptomelane. Aliquots of the prepared cryptomelane were calcined in air for 2 h at 350 °C, 400 °C, 500 °C, and 600 °C.

2.1.2. Reflux method

The reflux method used here was described by Frias et al. [46] and by Valente et al. [47]. 11 g of manganese acetate was added to 40 mL of deionized water. 5 mL of glacial acetic acid was added to the solution. This solution was brought to a boil in a refluxing apparatus with vigorous stirring. In a separate beaker, 6.5 g of $KMnO_4$ was added to 150 mL of deionized water. This $KMnO_4$ solution was then added slowly to the refluxing solution and allowed to react for 24 h under refluxing conditions. After cooling, the black precipitate was filtered, washed with deionized water, and dried. These samples were then calcined at 450 °C for 24 h.

2.1.3. Milling method

The milling method, or solid state method, used here was described by Ding et al. [48], Li et al. [49], and Valente et al. [47]. In brief, $KMnO_4$ and Mn acetate were placed in a mortar in a molar ratio of 2:3. The materials were ground for several minutes until the mixture was a gray color and uniform texture. The mixtures were then placed in a glass vial and heated to 80 °C for 24 h. The

Download English Version:

<https://daneshyari.com/en/article/147141>

Download Persian Version:

<https://daneshyari.com/article/147141>

[Daneshyari.com](https://daneshyari.com)