

Liquid Phase Decomposition of Organic Substrates on Birnessites

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Catalytic activity of layered birnessite type manganese dioxide for liquid phase decomposition of organic substrates is reported in this paper. Oxidation of acetone, methanol and 2-propanol have thus been studied.

Introduction

Birnessite is a common manganese dioxide found in soils, ore deposits and marine manganese nodules¹⁻⁵. Due to their octahedral layer (OL) structure, birnessite-type materials have been designated A-OL-1 in which A identifies the interlayer cation⁶. The OL-1 designation usually refers to 7Å birnessite, but other layered manganese oxides can also be represented, for example, as 5.5 or 10A-OL-1 materials.

Despite their near stoichiometry, birnessites are known to have variable and therefore poorly defined elemental composition. The birnessite formula is generally expressed as $A_x Mn_{2+y} (H_2O)_z$ in which A typically represents an alkali metal cation. The average oxidation state of the mixed valent manganese normally, falls between 3.6 and 3.8, which represents a predominance of Mn(IV) with minor amounts of Mn(III). There is also speculation over the presence of some Mn(II).

The microporous nature, large surface area and ion exchange properties of birnessites⁷ together with their relative abundance in marine manganese nodules prompt their application as catalyst for organic oxidations. The Indian Ocean contains huge deposits of marine manganese nodules. Birnessites and other related OL-1 materials are also key synthetic precursors for manganese oxides with tunnel structures, hollandites and todorokites.

Various methods are available for the synthesis of birnessite type manganese dioxides. Sol gel redox synthesis has received considerable attention in the recent past⁸⁻¹². In the present work, sol gel derived form of manganese dioxides has been investigated for their catalytic activity for oxidation of organic substrates.

Materials and Methods

Unless otherwise specified, all chemicals used were E Merck GR grade products. Double distilled water was used in preparing the solutions.

Preparation of Birnessite

A solution of 6 g of potassium permanganate in 50 ml of 5 per cent KOH was added quickly to a solution of 10-12 g of hydroxylamine in 50 ml of 20 per cent KOH. The resulting solution was vigorously stirred for about 3 min and then allowed to stand when a reddish brown sol formed which when left to remain at room temperature thickened to form a deep brown gel within about 2 h. Upon drying at 393 K the gel yielded a porous black mass. Calcination of this mass at 673 K gave a black powder. The powder was washed several times with distilled water and then dried at 393 K.

The resulting black powder (yield = 2.3g) was characterized to be a potassium birnessite. Sodium birnessite was prepared in a similar manner using sodium permanganate in the place of potassium permanganate. The analysis revealed a formula of $K_{1.44} Mn_6 O_{11.7} \cdot H_2O$ for potassium birnessite; $Na_4 Mn_{14}$

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$O_{27.9}H_{20}$ for sodium birnessite. A manganese oxidation state of respectively 3.72 and 3.57 was revealed by iodometric titration¹³. Ion-exchanged birnessites were prepared by shaking the sodium birnessite in the salt solution containing bismuth, zinc or lead ions. The choice of the sodium precursor was owing to the reported difficulty of exchanging potassium ions.

The surface area of the potassium, sodium, lead, zinc and bismuth birnessites were respectively 55.5, 40.2, 55.0, 57.0, 67.0 m²/g. XRD patterns were recorded on a Philips X-ray diffractometer using Cu K α radiation.

Decomposition Study

The catalytic runs were carried in a 3-necked round bottom flask immersed in a thermostated bath and equipped with a condenser, a thermometer and a magnetic stirrer. In a typical experiment 50 ml of the reactant and 5 g of the catalyst were mixed in the flask and heated to a desired temperature under continuous stirring. Small samples were taken out at regular intervals using a syringe for analysis by gas chromatography using a Chemito GC 8610 HR instrument. Carbon dioxide and water were identified qualitatively.

Cyclic Voltammograms were recorded on a PAR model 173 potentiostat/galvanostat model 176 current to voltage converter and a model RE 008 XY recorder using a home assembled cell. The working electrode consisted of a gold foil (2.25 cm² area) on which the sample mixed with 25 weight-percent graphite was pressed. The electrolyte was 0.1 M KCl buffered at pH 7.2.

Results and Discussion

In the present study sodium, potassium, bismuth, lead and zinc exchanged manganese dioxides prepared by the present sol gel redox process have been used for the oxidation of methyl alcohol, acetone and 2-propanol in a liquid phase oxidation reaction. The results obtained are presented in Tables 1 to 3 which show superior catalytic activity of these materials as compared with that of pyrolusite (Table 4). A further point of interest is the influence of the cations. Bismuth exchanged MnO₂ offers the highest conversion followed by zinc and lead counterparts. Sodium and potassium precursors exhibit low catalytic activity.

Parida *et al.*¹⁴⁻¹⁷ who have studied the gas phase oxidation of organic substrates on Indian Cocco manganese nodules have proven that δ -MnO₂ type is the active component in marine manganese nodules.

Table 1—Features of oxidation of methyl alcohol on birnessites. Reaction time: 6 h.

Cation in the birnessite	Reaction temp, K	Product	Per cent conversion
Na ⁺	333	CO ₂ , H ₂ O, HCOOH	30
K ⁺	333	CO ₂ , H ₂ O, HCOOH	30
Pb ⁺²	333	CO ₂ , H ₂ O, HCOOH	45
Zn ⁺²	333	CO ₂ , H ₂ O, HCOOH	47
Bi ⁺³	333	CO ₂ , H ₂ O, HCOOH	53

Table 2—Features of oxidation of acetone on birnessites. Reaction time: 6 h.

Cation in the birnessite	Reaction temp, K	Product	Per cent conversion
Na ⁺	323	CO ₂ , H ₂ O	41
K ⁺	323	CO ₂ , H ₂ O	41
Pb ²⁺	323	CO ₂ , H ₂ O	48
Zn ²⁺	323	CO ₂ , H ₂ O	44
Bi ³⁺	323	CO ₂ , H ₂ O	54

Table 3—Features of oxidation of 2-propanol on birnessites. Reaction time: 6 h.

Cation in the birnessite	Reaction temp, K	Product	Per cent conversion
Na ⁺	353	CO ₂ , H ₂ O, acetone	38
K ⁺	353	CO ₂ , H ₂ O, acetone	38
Pb ²⁺	353	CO ₂ , H ₂ O, acetone	47
Zn ²⁺	353	CO ₂ , H ₂ O, acetone	49
Bi ³⁺	353	CO ₂ , H ₂ O, acetone	57

Table 4—Features of oxidation of methyl alcohol, acetone and 2-propanol on Pyrolusite. (≤ 5 microns). Reaction time: 6 h.

Reaction	Reaction temp, K	Product	Per cent conversion
methyl alcohol	333	HCHO	8
acetone	323	CO ₂ , H ₂ O	5
2-propanol	353	acetone	12

All the manganese dioxide samples prepared in the present study have been proven to be birnessite type $\delta\text{-MnO}_2$ by X-ray analysis. A typical birnessite material exhibits two major peaks in the XRD spectrum, at 7.0\AA (002) and 3.5\AA (210); the peak at 7.0\AA is of great importance and represents the adjacent Mn-Mn distance¹⁸ (Figure 1). The poor catalytic activity of pyrolusite is thus owing to its non-birnessite type structure. The role played by the cations of the birnessite as observed in the present study indicates their participation in the catalytic mechanism. Oxidation of combustible materials is known to be catalyzed by manganese oxide composition involving transition metals¹⁹ as in marine manganese nodules in which metals like lead, bismuth and zinc are also minor components.

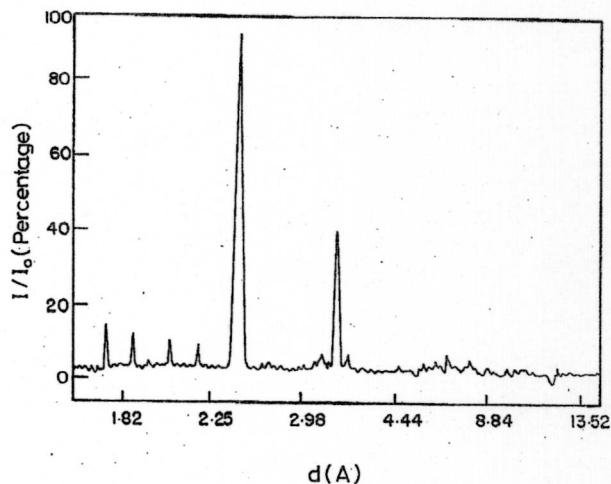


Figure 1—XRD pattern of potassium birnessite

The birnessites employed in the above studies, showed distinct changes in their features. The most explicit of the changes was the development of purplish tinge in the colour. Estimation of manganese valency showed decrease in Mn(IV) content and increase in Mn(III) and Mn(II) content. The cyclic voltammograms presented in Figure 2 provided support to the changes in the redox behavior of birnessite on account of the catalytic activity for decomposition of organic substrates. In Figure 2, curve a is the cyclic voltammogram of potassium birnessite, a prominent redox couple is seen in the cyclic voltammogram with an anodic peak potential, E_{pa} at 3.35V and a cathodic peak potential E_{pc} at 2.75V. The couple corresponds to the reduction of Mn(IV) ions to Mn(III)²⁰. The couple exhibits a constancy of E_p values at different sweep rates with $i_{pa} = i_{pc}$ and $E_p = 55\text{mV}$ characteristic of 1e process. In birnessites, the oxidation state of manganese normally falls between 3.6 and 3.8 (ref. 21-23) which represents a predominance of Mn(IV) with minor amounts of Mn(III). There has also been some speculation over the presence of Mn(II)²¹⁻²². The shoulders exhibited by the cyclic voltammogram of Figure 2 might be representative of such coexistent species. In the cyclic voltammogram of spent birnessites, there is a reduction in peak current of Mn⁴⁺/Mn³⁺ couple and the shoulders owing to Mn³⁺ and Mn²⁺ reduction anodes are higher. This observation supports that Mn⁴⁺ oxidation state was chiefly responsible for the oxidation of organic substrates.

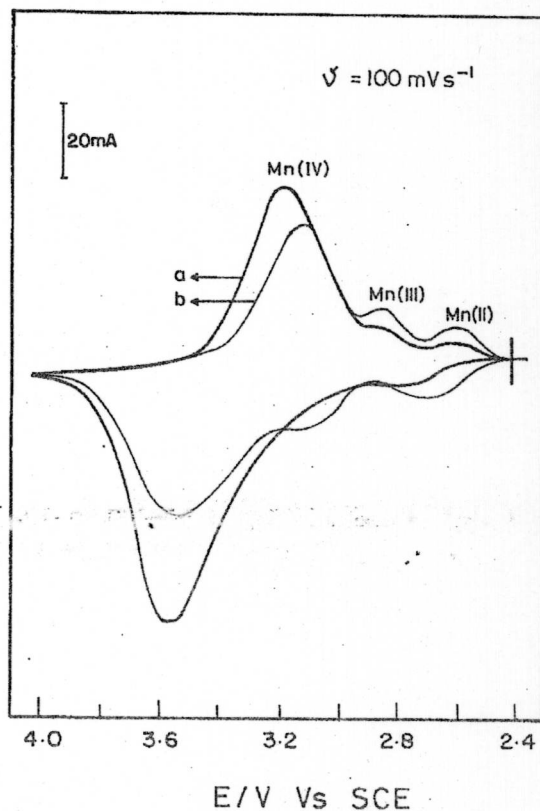


Figure 2—Cyclic voltammogram of potassium birnessite before (a) and after (b) subjected to the catalytic decomposition of methanol

In the present study, evidence for the participation of non-transition metal ions like Pb^{2+} , Zn^{2+} and Bi^{3+} are obtained. The fact that their influence is strong, indicates that the catalysis may

proceed probably through an alkoxide intermediate. However a detailed study is essential for arriving at the mechanism.

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