

APPLICATION OF DIFFERENTIAL SCANNING CALORIMETRY TO THE REDUCTION OF SEVERAL MANGANESE OXIDES

C. González¹, J. I. Gutiérrez¹, J. R. González-Velasco¹, A. Cid²,
A. Arranz² and J. F. Arranz²

¹Chemical Engineering Department, Sciences Faculty, University of Basque Country, 48080 Bilbao

²Analytical Chemistry Department, Pharmacy Faculty, University of Basque Country, 01006 Vitoria, Spain

Abstract

The aim of this work was to study the thermal transitions of several manganese oxides (MnO, MnOOH, Mn₂O₃, Mn₃O₄ and MnO₂) under reducing conditions. Differential scanning calorimetry (DSC) was used to analyse the transitions of some oxides into others. A comparison of the behavior of the synthetic samples with that of a natural manganese dioxide demonstrated that DSC is a quick tool for the distinction of natural manganese dioxide from synthetic γ -MnO₂ from other manganese oxides.

Keywords: DSC, manganese oxides, reduction

Introduction

Manganese oxides have been the subject of many studies in consequence of their electrochemical and industrial applications [1–3]. Increasing attention has also been devoted to determining the transformation of various manganese oxides into others. It is important to study the behavior of these compounds during reduction under a hydrogen atmosphere with a view to understanding the electric discharge observed by voltammetric analysis [4]. Natural manganese dioxide (NMD) is generally a mixture of different oxides and can be applied as cathodic material in primary cells. The term gamma-manganese dioxide is applied to a series of hydrated manganese dioxides of moderate crystallinity that are suitable for battery purposes. These occur in nature with the mineral nsutite and have optimum activity for use in dry cell batteries. The gamma variety can appear composed of irregular structural combinations of β -MnO₂ (single-chain) and ramsdellite (double-chain) components. The crystal structure of NMD is similar to that of nsutite. Its phase is γ -MnO₂ and shows a region of simple and double chains of edgeshare (MnO₆) octaetra.

This work forms part of a more extensive study of the thermal transformations of some oxides into others [5, 6]. DSC is considered a convenient tool with which the various transitions of the oxides may be understood. The objective of this part is to apply DSC to observe the changes and phase transitions that occur during heating under reducing conditions in synthetic MnO, MnOOH, Mn₂O₃ and Mn₃O₄ samples. Their behavior has been compared with that of a NMD sample from Gabon and that of a synthetic γ -MnO₂.

Experimental

The different manganese oxides were prepared by procedures described previously [6]. DSC was carried out with a Perkin Elmer DSC-4 calorimeter, using a linear heating rate of 20°C min⁻¹ from 50 to 500°C, and a gas flow of 30 cm³ min⁻¹. The calorimeter was previously calibrated with indium as standard. The reducing atmosphere was a 1:3 mixture of hydrogen in nitrogen, the same total flow being maintained. The gases used had a purity of 99.998%.

X-ray diffractograms (XRD) were recorded to characterize the prepared oxides. They were recorded stepwise (5°, 60 s) at room temperature, with a Philips PW 1710 diffractometer equipped with a copper anode generating CuK α radiation ($\lambda=1.5417$ Å), in the 2 θ range between 2 and 70°.

Results and discussion

Table 1 lists the main structural data obtained from the XRD analyses and the corresponding card of each oxide. NMD is a mineral characterized as gamma-phase manganese dioxide contaminated by a very little of the beta-phase. NMD gave a diffractogram reflecting a crystalline structure very similar, but not equal to that of γ -MnO₂. To compare the energetic changes between γ -MnO₂ and NMD (both used in the preparation of batteries), a synthetic γ -MnO₂ was prepared from manganese sulfate by an electrolytic procedure with titanium anodes [6].

Table 1 Structural characteristics of the synthetic and natural manganese oxides, identified by comparing the experimental results with the reference data of X-ray diffractometry

Oxide	Structural characteristics	Reference data XRD
MnO	Manganosite: cubic system	JCPDS 7-0230
Mn ₃ O ₄	Manganosic oxide: cubic system	JCPDS 4-0732
Mn ₂ O ₃	Partridgeite: cubic system	JCPDS 10-69
MnOOH	Manganite: monoclinic system	JCPDS 18-805
γ -MnO ₂	Gamma manganese dioxide: tetragonal system	JCPDS 14-664
NMD	Nsutite (Type gamma manganese dioxide: tetragonal system)	JCPDS 4-0779

The reduction of manganese dioxide occurs by a complex mechanism in which several stages are involved. This reduction can be due to heating or to a reducing agent such as hydrogen. The temperature of each stage depends on the oxide preparation conditions, and the operational parameters during reduction. Manganese dioxide reduction can be described as follows:

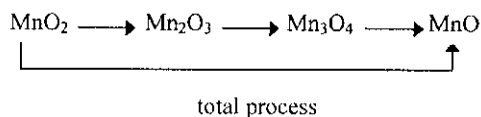


Figure 1 depicts DSC curves for the studied oxides. It can be observed that MnO does not give peaks in the studied temperature range. Mn_2O_3 displays one exothermic peak close to 500°C . This is due to the transition to MnO. The observed transformation peak corresponding to Mn_3O_4 appears at a higher temperature than the studied maximum (500°C) and relates to the transition to MnO. For MnO_2 the reduction takes place in two steps. The first, at 296°C , corresponds to the transformation to Mn_2O_3 (the associated energy of the process is 535 cal g^{-1}). The second step is due to the transition from Mn_2O_3 to MnO. The onset temperature is 378°C and the energy of the process is 223 cal g^{-1} . MnOOH is reduced progressively into several compounds. The first reduction occurs at around 250°C . First, MnOOH is reduced to Mn_5O_8 and this is quickly transformed to Mn_2O_3 . At higher temperature (348°C), Mn_2O_3 is reduced to a mixture of Mn_3O_4 and MnO. The nature of each manganese oxide after the transformation steps was identified by comparing the results with those presented in a previous paper [5], where the

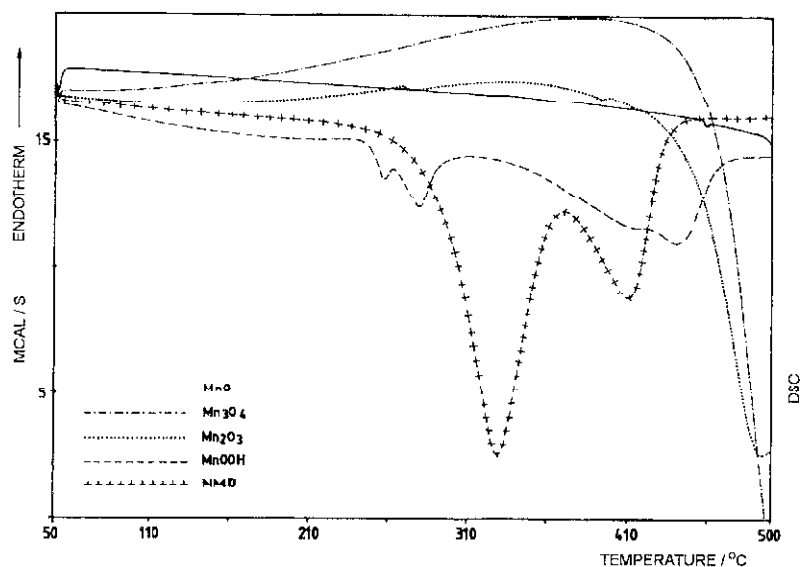


Fig. 1 DSC curves for several manganese oxides in a reducing atmosphere

thermal transformations of manganese oxides in several atmospheres were analysed by thermogravimetry.

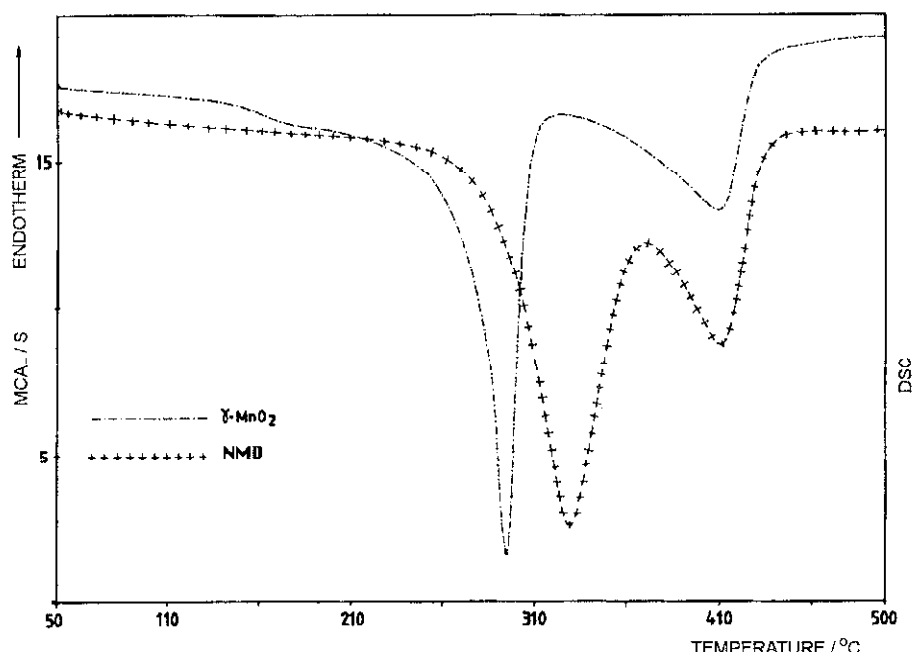


Fig. 2 Comparison of DSC curves for NMD and synthetic γ - MnO_2 samples under reducing conditions

The DSC plot for γ - MnO_2 was compared with that for the NMD; both are represented in Fig. 2. It can be observed that the first transition, from MnO_2 to Mn_2O_3 , occurs at lower temperature for the synthetic sample (the onset temperature is 281°C , while for the NMD the temperature is 296°C). This temperature difference (15°C) can be explained by the presence of beta-phase contaminating the gamma-phase structure. The associated energies are very similar (541.4 and 535.3 cal g^{-1} , respectively). All the observed transitions were exothermic, as typical of reduction processes.

The second transition, the reaction from Mn_2O_3 to MnO , exhibits an onset temperature of 378°C for the NMD, and of 352°C for the synthetic dioxide. The temperature shift may be explained by the enthalpy changes of the interaction with its polymorphic transition. This indicates that the NMD reduction process takes place with more difficulty than for γ - MnO_2 , due to the relative thermodynamic stability of the beta-phase in the lattice. A large difference is found in the associated energies (223.5 for the NMD and 336.1 cal g^{-1} for the synthetic material). These results indicate that DSC plays a good role in distinguishing synthetic manganese dioxide samples from natural ones.

DSC allowed an unambiguous identification of various manganese oxides; several of them may be present in NMD. These results were obtained on various samples and demonstrate the value of DSC for the structural characterization of these compounds.

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