DSC Study of Some Manganese Oxides under Reduction

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Abstract : In this paper present work is to DSC study of some manganese oxides under reduction. The natural Manganese dioxide (NMD) is generally a mixture of different oxides like MnO, MnOOH, Mn_2O_3, Mn_2O_4 and MnO_2 under reducing conditions. Differential scanning calorimetric (DSC) was used to analyse the transitions of some manganese oxides into others. The paper also aim to study the comparative behaviour of the synthetic samples with that of a NMD demonstrated that DSC is quick tool for the distinction of NMD from systhetic MnO_2 from other manganese oxides.

Keywords : DSC instrument, NMD, Manganese oxides, Reduction.

I. INTRODUCTION

The natural Manganese dioxide (NMD) is generally a mixture of different manganese oxides and can be applied as cathode material cells. The manganese oxides have been the subject of any studies in consequence of their electrochemical and industrial apllication[1-3]. The increasing attention has also been devoted to determining the transformation of various manganese oxides into others. These is most important to study the behaviour of these compounds during reduction condition under a hydrogen atmosphere with in a view to understanding the electric discharge observed by voltammetric analysis[4].

The MgO is frequently obtained from calcined dolomite by means of the pattinson procedure and the rate of kinetic parameter rate of hydration of MgO increases also[5]. The term gamma-manganese dioxide is applied to a sequences of hydrated manganese dioxides of moderate crystallinity that are stictable for battery purposes. These occur in nature with the mineral nsutite and have optimum a activity uses in dry cell batteries. Te gamma variety can appear composed of irregular structural combination of β-MnO_2 (single chain) and tramsdellite (double-chain) components. The crystal structure of NMD is similar to crystal structure of nsutite. Its phase is γ-MnO_2 and shows a region of simple and double chain of edge share (MnO_6) octahedra.

DSC is considered a convenient tool with which the various transitions of the oxides maybe understand. The main 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, MnO_2, MnOOH and Mn_3O_4 samples. Their behaviour has been compared with that of a NMD sample from Gabon and that of a synthetic γ-MnO_2 compounds.

II. EXPERIMENTAL PROCEDURES

In the inorganic and Analytical Research Laboratory the different manganese oxides were prepared by standard procedures. DSC was carried out with a DSC- 20 Mettler TA-4000 calorimeter instrument using a linear heating rate of 20^0C min^{-1} from 50 to 500^0C and a gas flow of 30 cm^3 min^{-1}. The DSC calorimeter was previously calibrated with Indian as standard. The reducing atmospheres were a 1:3 mixture of hydrogen in nitrogen, the same total flow being maintained. The gas used has a purity of 99.998%.

The second procedures of X-ray diffractograms (XRD) were recorded to characterize the prepared oxides. They were recorded stepwise (5^0, 60s) at room temperature, with a Philips PW 1710 dittractometer equipped with a copper anode generating CuKα radiation radiation (λ=1.5417A^0) in the 2Θ range between 2^0 and 70^0.

III. RESULTS AND DISCUSSION

The main structural characteristics data of different manganese oxides data obtained term the XRD analysis reference data shown in the given below table No. 1.

TABLE No.-1

Oxide	*Structural Characteristics*	*XRD analysis Reference data*
MnO	Manganosite: cubic system	JCPDS 7-0230
Mn_3O_4	Manganosic oxide: cubic system	JCPDS 4-0732
Mn_2O_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 NMD is a mineral characterized as gamma phase manganese dioxide contaminated by a very little of the beta phase. The NMD gave a diffractogram reflecting a crystalline structure very similar, but not equal to that of γ-MnO_2 . To compare the studies temperature range. Mn_2O_3 displays endothermic peak close to 500^0 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 (500^0C) and related to the transition to MnO. The MnO_2 the reduction takes place in two steps. The first step at 296^0C corresponding to the transformation to Mn_2O_3. The second step is due to the transitions from Mn_2O_3 to MnO. The onset temperature 378^0C and the energy of the process is 223 cal g^{-1}. The MnOOH is reduced progressively into some compounds. The first reduction occurs at around 250^0C. The MnOOH is reduced to Mn_50_8 and this is quickly transformed to Mn_2O_3. At higher temperature at 348^0C. The Mn_2O_3 is reduced to a mixture of Mn_50_4 and MnO. The nature of each manganese oxide after the transformation steps was identified comparing the results with those presented in a previous work where the thermal transformation of manganese oxides in several atmospheres were analysed by thermogravimetry enervative changes between γ-MnO_2 NMD, a synthetic γ-MnO_2 was prepared from manganese sulphate by an electrolytic procedure with titanium anodes.

The reducing conditions of manganses dioxide occur by a complex mechanism in which several stages are involved. This reduction can be due to heating reducing agent such as hydrogen. The temperature of each stage depends on the oxides preparation conditions, and the operational parameters during reduction manganese dioxide reduction can be given below

$$MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$$

Total Process

The DSC instrument plots a curves graph for some manganese oxides in a reducing atmosphere and conditions which shown in figure No. 1 as given below:

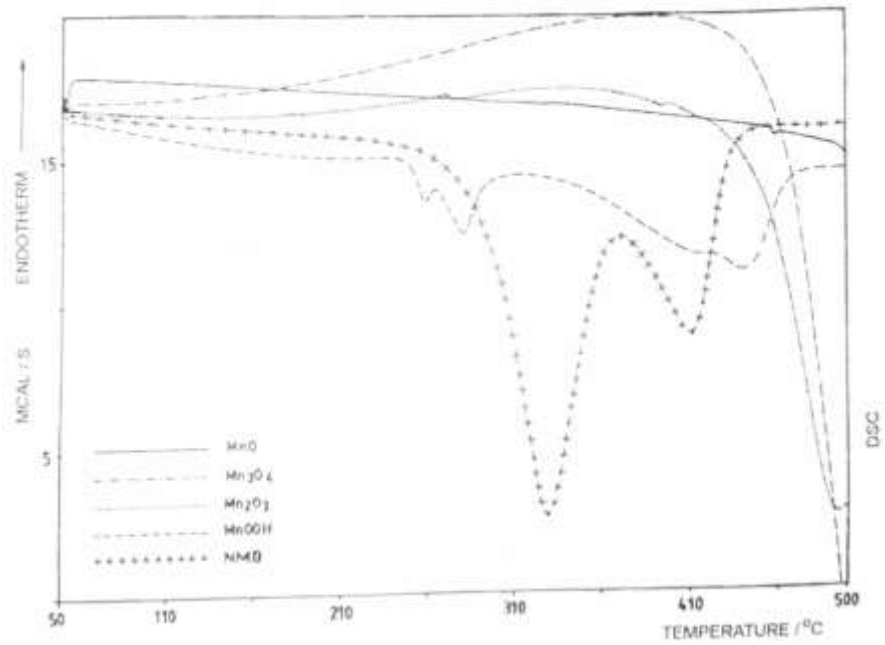

Fig. 1 : DSC curves for several manganese oxides in a reducing atmosphere

It can be above figure observed that MnO does not give peaks in difference 15^0C 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 peaks, as typical of reduction processes.

The Second transition, the reaction from Mn_2O_3 to MnO, exhibits an onset temperature of 378^0C for the NMD and of 352^0C for the synthetic dioxide. The temperature shift may be explained by the enthalpy change 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. At large difference is found in the DSC instrument plot a curve graph represent the comparison of DSC curves for NMD and synthetic γ-MnO_2 samples under reducing conditions shows in figure No. 2 as given below:

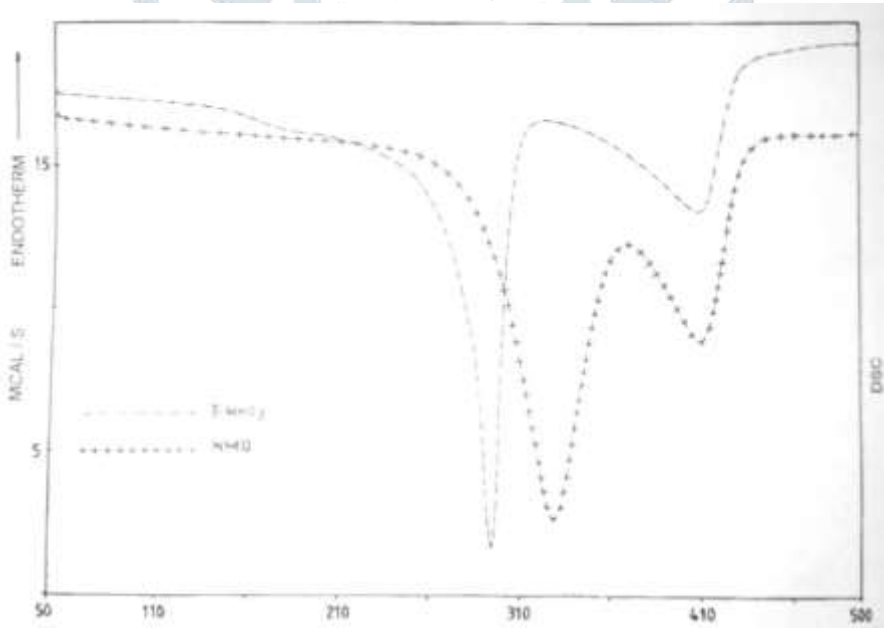

Fig. 2 : Comparison of DSC curves for NMD and synthetic γ-MnO_2 samples under reducing conditions

The above graph curves in figure No.-2 can be observed that the first transition, from MnO_2 to Mn_2O_3, occurs at lower temperature for the synthetic sample i.e., the onset temperature 281^0C while the

NMD the temperature is 296^0C. This temperature associated energies, 223.5 for the NMD and 336.1 Cal g^{-1} for the synthetic manganese dioxide samples from natural ones.

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

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