CHEMISTRY LETTERS, pp. 1079-1080, 1978. Published by the Chemical Society of Japan

A NEW COMPOUND OF δ-MnO_2 FAMILY; δ-MnO_2(II)

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Black precipitate of so-called δ-MnO_2 was found usually to be a mixture of two different kind of compounds (δ-MnO_2(I) and δ-MnO_2(II)). Crystallographic conversion took place between these compounds in the presence of their mother liquid.

Black precipitate, which was obtained by oxidizing $Mn(OH)_2$ suspension in concentrated NaOH alkaline solution at room temperature, was called usually δ-MnO_2. Formation condition, chemical and physical properties of the compound were reported by many authors.1-8) Recent study of R.Giovanoli et al claimed that the compound should be described as $Na_4Mn_{14}O_{27}$ $9H_2O$ instead of δ-MnO_2 having a orthorombic unit cell (a=8.54, b=15.39 and c=14.26Å).6-8) But results of these reports were not consistent with each other. We have carried out extensive X-ray diffraction study and found that so-called δ-MnO_2 was a mixture containing two compounds and some curious crystallographic conversion took place between these two compounds. Experimental results were as follows.

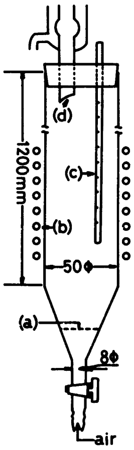

Fig. 1 Schematic drawing of reaction tube. The tube was constructed from pyrex (a) glass filter (b) heater (c) thermometer (d) cooling tube

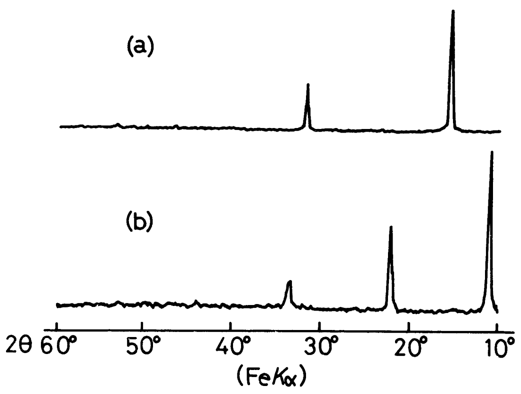

Fig. 2 X-ray diffraction patterns (a) δ-MnO_2(I) (b) δ-MnO_2(II)

The starting suspension of $Mn(OH)_2$ was prepared by dissolving 50g of $MnSO_4$ $5H_2O$ in 0.5 l distilled water and then adding 0.5 l of 5N-NaOH solution to it. Obtained suspension of $Mn(OH)_2$ was poured in a reaction tube (Fig. 1) and diluted with oxygen free water to 1.5 l. Suspension of $Mn(OH)_2$ was oxidized with air (800/h) at room temperature. White precipitate of $Mn(OH)_2$ was gradually oxidized to black δ-MnO_2. About an hour later oxidation was completed. Small amount of precipitate was extracted from the suspension for X-ray measurement. Then extraction of sample was repeated at interval of desired time. During the procedure aeration was continued to agitate the suspension. In X-ray measurement care should be taken not to dry up samples from its mother liquid for avoiding chemical and or crystallographic conversion of samples. In most cases obtained X-ray diffraction pattern of a sample was made of two sets of peaks. One of them coincides with patten of $Na_4Mn_{14}O_{27}9H_2O$ and the other is entirely new one (hereafter we describe the former as δ-MnO_2(I) and the latter as δ-MnO_2(II), respectively). The X-ray diffraction patterns of δ-MnO_2(I) and

δ-MnO$_2$(II) are given in Fig. 2. Moreover δ-MnO$_2$(I) and δ-MnO$_2$(II) showed time dependent crystallographic conversion between each other in their mother liquid. The observed characteristic example of time dependent conversion was shown in Fig. 3. In this figure ratio of δ-MnO$_2$(II) to δ-MnO$_2$(I) in a sample is represented with relative main peak intensities of X-ray diffraction pattern (2θ = 11.2^o and 2θ =16.2^o using FeKα). Repetition of experiment showed conversion degree of δ-MnO$_2$(I) to δ-MnO$_2$(II) or vice versa was usually not so complete as the case of Fig. 3. In most cases an amount of δ-MnO$_2$(I) in a sample was between 20~80% and showed time dependent fluctuation within the range of the figures. Suspension of so-called δ-MnO$_2$ was heated, time dependent fluctuation between two compounds was centering around more δ-MnO$_2$(I) rich portion (if suspension was heated in the presence of Mn(OH)$_2$ contamination of Mn$_3$O$_4$ was observed). Above 70^{o}C only δ-MnO$_2$(I) was observed throughout experimental period (48h). Cooling of suspension below room temperature had little effect on conversion between two compounds. Although it takes about 3 hour of time in Fig.3 , cycle of conversion period of δ-MnO$_2$(I) to δ-MnO$_2$(II) was rather irregular in usual. We could determine neither chemical composition nor crystal structure of δ-MnO$_2$(II), for the compound being so unstable without its mother liquid that freeing from mother liquid by filtration inducing partial structure conversion to δ-MnO$_2$(I). Both fragility of δ-MnO$_2$(II) and two dimensional-like crystal structure of δ-MnO$_2$(I) strongly suggest mutual conversion of crystal structure in mother liquid was induced by egress and ingress of H$_2$O or OH$^-$ molecule at skeleton structure of a crystal lattice. But the problem is left behind.

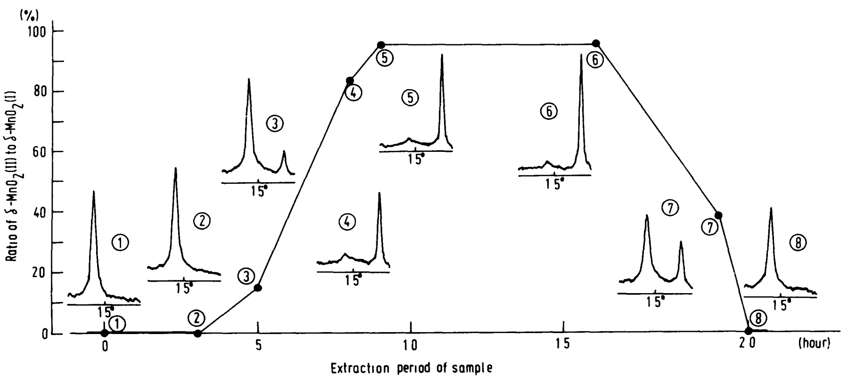

Fig. 3 Time dependent crystallographic conversion between δ -MnO$_2$(I) and δ-MnO$_2$(II) in their mother liquid at room temperature. Portion of X-ray diffraction patterns of the samples are also given in the figure (δ-MnO$_2$(I) 2θ =16.2^o and δ-MnO$_2$(II) 2θ =11.2^o)

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(Received July 17, 1978)