Low-temperature stabilization of pure MnO

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Abstract. A technique has been worked out for stabilizing polycrystalline MnO against oxidation in air without dopants and without exceeding a temperature of 800°C in the process. The material is active though highly resistant to oxidation.

Keywords. Stabilized MnO; active MnO; pure MnO.

1. Introduction

MnO, the lowest oxide of manganese, is well known, in a polycrystalline form, to pick up oxygen from air and get oxidized easily even at room temperature. The oxide can however be dead burnt by heating at 1000°C for some hours in an inert atmosphere or hydrogen and thereby stabilized against oxidation at room temperature (Hay *et al* 1934; Cheetham and Hope 1983). The stabilization of MnO by processing below 800°C has also been achieved by doping with other oxides, particularly ZnO (Deshpande *et al* 1978; Deshpande and Murthy 1981). A low-temperature stabilization of MnO without any dopants does not appear to have been worked out so far. The low-temperature of processing is necessary to keep the oxide active enough for purposes of catalysis and solid state reaction with other oxides; the absence of dopants is obviously necessary to avoid unwanted impurities. The present paper deals with the stabilization of pure polycrystalline MnO by processing below 800°C and maintaining the oxide in a finely divided state.

2. Experimental

The experimental set up is illustrated in figure 1 which is a somewhat simplified version of that described in an earlier paper by one of the present authors (Deshpande and Murthy 1981). The system is perfectly gas-tight and previously tested for holding vacuum, though evacuation is not needed in this work. The figure is self-explanatory. A higher oxide of manganese prepared by heating precipitated manganous oxalate at 300°C in air is taken in platinum boat, 5, while an excess of reduced iron powder is taken in silica boats, 4, placed in the furnace tube in the vicinity of the platinum boat. It is assumed that the iron gets converted to Fe_3O_4 with the available oxygen in the higher oxide of manganese taken, and double the amount of iron calculated on this basis is

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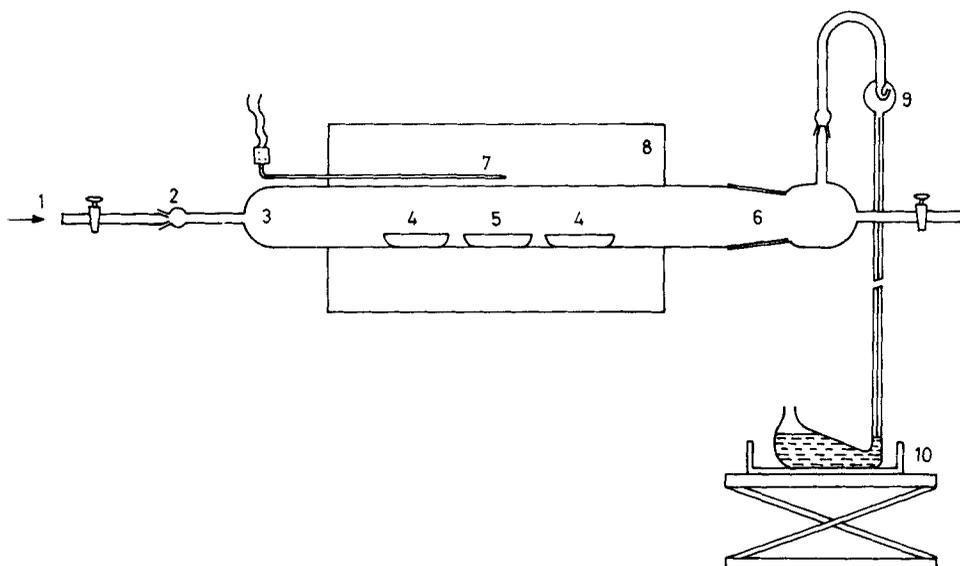
Figure 1. Preparation unit for MnO: (1) gas inlet; (2) B-14 silica to pyrex joint; (3) quartz tube (50 mm dia); (4) iron powder in Silica boats; (5) Mn_2O_3 in platinum boat; (6) B-55 silica to pyrex joint; (7) thermocouple; (8) Kanthal-wound furnace; (9) mercury manometer/cut off; (10) petri-dish with foam rubber cushion.

taken in the silica boats. Care is taken to avoid any contamination of the oxide of manganese with the iron. It helps to dilute the iron powder a little with an inert material such as alumina to avoid the formation of iron clusters on heating. The unit is then assembled as shown in the figure and flushed with cylinder nitrogen for 10–15 minutes with the gas entering at 1 and bubbling out of the manometer 9. The inlet stopcock is then closed, the temperature of the reaction tube is raised to 750–800°C and the oxide of manganese is soaked at this temperature for about eight hours in a static atmosphere of cylinder nitrogen with the reduced iron also present in the system. The furnace is then switched off and cooled to room temperature. The resulting oxide of manganese in the platinum boat is taken out by opening ground joint 6.

An x-ray powder pattern of the material completely tallied with that of MnO. The oxide of manganese was checked for any active available oxygen by heating it with hydrochloric acid in a current of oxygen-free nitrogen (Schenk 1963), and in a closed system previously flushed thoroughly with the same gas. The gas was allowed to bubble through a solution of potassium iodide and starch in the same closed system. The starch iodide showed no change of colour indicating the absence of Mn^{3+}. An x-ray photoelectron spectrum (xps) of the oxide of manganese gave the expected peaks at 640·9 and 652·5 eV corresponding to $2p_{3/2}$ and $2p_{1/2}$ core levels of Mn^{2+}. The peaks at 641·7 and 653·3 eV, characteristic of the same core levels of Mn^{3+}, were particularly looked for and found to be absent (Rao *et al* 1979); in fact, there were no other peaks. A known weight of this oxide of manganese was heated overnight in a muffle furnace at 900°C, cooled in a desiccator and weighed. The increase in weight corresponded to 7·52% which was just the expected value for oxidation of MnO to Mn_3O_4. A thermogram of this oxide of manganese with a heating rate of 10°/min showed an increase in weight only after 440°C. When, however, the thermogram was

repeated with a slower heating rate of $3°/min$, there was a faintly perceptible gain in weight only above $200°C$, though even then the increase in weight upto $400°C$ was less than 0.5%. A diffuse reflectance spectrum of the substance gave absorption peaks at 616, 485 and 422 nm in complete accord with the absorption spectrum of MnO single crystals reported earlier (Pratt and Coelho 1959). A scanning electron micrograph of this MnO is given in figure 2. Every one of the properties of MnO given above was rechecked after storing the powder in air without any special precautions for three months, and found to be fully reproducible.

The MnO prepared as above was mixed with a little $NH_4 HCO_3$ and heated on a water bath side by side with another sample of the same MnO unmixed with $NH_4 HCO_3$. It was found that as soon as the bicarbonate started decomposing, the MnO mixed with it got oxidized and turned black; while the MnO without $NH_4 HCO_3$ remained olive green as before and answered no test for Mn^{3+}.

3. Discussion

The reduced iron powder acts as an oxygen getter and completely takes up the available oxygen in the higher oxide of manganese as well as the cylinder nitrogen initially filling the reaction tube. Whatever oxide of iron is formed in the process is incapable of reoxidizing the MnO; and this is as it should be since it is well known that while Fe^{2+} can reduce Mn^{3+}, Mn^{2+} is never known to reduce Fe^{3+}. The chemical test for the absence of available oxygen, the expected weight increase in air at $900°C$ to Mn_3O_4, the xps, the x-ray powder pattern and the diffuse optical reflectance spectrum confirm the formation of MnO and the absence of Mn^{3+} in it. The fact that the substance could stand all these tests after a lapse of three months of storage in air shows the excellent keeping qualities of this MnO. The thermograms show that this MnO is not oxidized in
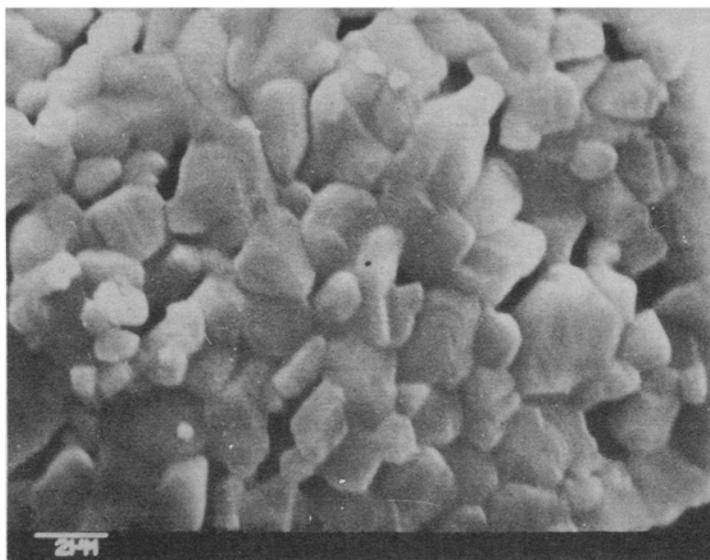

Figure 2. Scanning electron micrograph of MnO.

air upto 200°C while its oxidation even upto 400°C is very slow. The electron micrograph (figure 2) shows fairly uniform particles in the range of 2–4 μm. The escape of available oxygen from and through the higher oxide of manganese during the preparation breaks up the particles which are already small and active, being prepared by an effervescent decomposition of manganous oxalate in air below 300°C. Since the subsequent processing is carried out below 800°C, the grains are naturally as fine as figure 2 indicates. It is well known that the oxidation of MnO in air is nucleated and triggered off at a limited number of active sites at which an initial highly exothermic chemisorption of oxygen occurs (Hayward and Trapnell 1964). Apparently such highly active sites disappear in the process of soaking at 750 to 800°C for some hours, thereby conferring on the MnO the observed resistance to oxidation. All the same, the particles are still finely divided as mentioned earlier. The fact that this MnO loses its resistance to oxidation by the effervescent decomposition of NH_4HCO_3 mixed with it clearly confirms the above explanation of its observed stability. The gases (NH_3, CO_2 and H_2O) evolved from the decomposing bicarbonate disintegrate the MnO particles and expose fresh active sites at which chemisorption of oxygen can initiate the oxidation of MnO. Incidentally this gives a method of improving the activity of this MnO *in situ* provided the ambient atmosphere is inert.

This method of stabilizing MnO has obvious advantages over that of 'dead burning' above 1000°C, or doping with other oxides such as ZnO (Hay *et al* 1934; Deshpande *et al* 1978; Deshpande and Murthy 1981). The former process renders the MnO too inactive for any subsequent use while the latter introduces unwanted and sometimes harmful impurities besides being more cumbersome and difficult. In detail, the latter process (which was also worked out by one of the present authors, MNSM) involves an initial evacuation of the system, filling the system with oxygen-free nitrogen, maintaining a running current of the inert gas (scrupulously free from oxygen) all through the thermal decomposition of the oxalates and above all, thoroughly degassing the MnO in running high-vacuum in order to desorb the CO produced by the decomposition of the oxalates and tenaciously chemisorbed by the MnO (Hayward and Trapnell 1964). The heat of chemisorption of CO on MnO is as high as 64·4 k cal per mole at room temperature. The continuous flushing of the system in this process with oxygen-free nitrogen is necessitated by the tendency of the CO_2 evolved in the process to oxidize the MnO at the temperature of preparation (Sidgwick 1950). The degassing needed in the process is liable to remove part of the thermolabile ZnO and thereby change the stoichiometry of the solid solution arbitrarily. Furthermore, traces of CO may still remain with the MnO and this may be undesirable if the MnO has to be employed subsequently in the preparation of mixed oxide systems involving easily reducible metal oxides such as NiO, Fe_2O_3, CuO,CoO etc. The present process has none of these complications, involving no evacuation at any stage, employing only cylinder nitrogen (that too only during the initial flushing of the system) and requiring no degassing. Obviously, there is no possibility of any CO coming into the picture at any stage of this process.

4. Conclusion

The present paper deals with a novel method of stabilizing pure polycrystalline MnO employing a process not exceeding a temperature of 800°C. The MnO is surprisingly

resistant to oxidation in air while being sufficiently finely divided with particle sizes in the range of 2–4 μm. The particle size can be further reduced if necessary by heating *in situ* with NH_4HCO_3 in an inert atmosphere or in vacuum below 100°C. The process is very simple and gives an MnO totally free from harmful adsorbed gases.

While MnO chemisorbs carbon monoxide, oxygen and hydrogen very well (Hayward and Trapnell 1964), it has unfortunately not been used as a contact catalyst in reactions involving such gases. The reason is obviously that it has not been available in a stable and sufficiently active form. Many mixed oxide compositions and electronic ceramics – especially the technically very important professional soft ferrites which are actually manganous zinc ferrous ferrites—need pure MnO, without any Mn^{3+}, in a sufficiently active form to react efficiently with other oxides. The MnO made as described in this paper should prove useful for all such purposes.

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