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THERMAL SYNTHESIS OF HAUSMANITE VIA MANGANESE ALKOXIDE

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ABSTRACT

A hydrous non stochiometric hausmanite (with a Mn:O ratio between Mn_3O_4 and MnOOH) was synthesized by transformation of $MnCO_3$ or MnO_2 into crystalline manganese alkoxide (upon glyceration at 246°C), and subsequent hydrolysis of this alkoxide with boiling water. XRD, IR, DTA, etc. have been used to characterize this reactive compound with the lattice structure of Mn_3O_4 but containing also hydroxylated phases. The main sequence of events taking place when this peculiar material is heated in air, are:

$$\text{Synthetic hausmanite} \xrightarrow[\text{exothermic}]{630°C} Mn_2O_3 \xrightarrow[\text{endothermic}]{950°C} Mn_3O_4.$$

An endothermic event at ~1150°C is probably due to the common transition from tetragonal Mn_3O_4 to the cubic form.

INTRODUCTION

Some properties of manganese oxides, including catalytical applications, may depend on the method of preparation as well as on the originating material. The exploration of new routes for the preparation of these oxides is, therefore, interesting.

Most preparation methods of Mn_3O_4, so called hausmanite, utilize high temperature in the presence of air to effect the decomposition of manganous salts and subsequent oxidation to Mn_3O_4, or, alternatively, the decomposition and reduction of Mn_2O_3 or MnO_2 to Mn_3O_4. These and other procedures like electrolytic decomposition and hydrothermal techniques were briefly discussed by Bricker (1), who following earlier works (2) employed controlled oxidation of aqueous suspensions of $Mn(OH)_2$ in order to prepare Mn_3O_4.

Former works have shown that crystalline metal-glycerate complexes (alkoxides) resulted from a high temperature reaction between glycerol and oxides or other compounds of Co, Zn, Fe and Mn (3). Further works on synthetic and natural iron oxides or oxyhydroxides

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showed that the resulting iron glycerate complexes may undergo hydrolysis with boiling water, producing magnetic spinel oxides (4,5, 6). In the light of these studies we investigate here the synthesis of Mn_3O_4 and associated structures via manganese alkoxide intermediate, in a two steps reaction, using mainly manganous carbonate as starting material.

EXPERIMENTAL

Materials

All the reagents were of analytical grade supplied mostly by Fisher. CsI for infrared (IR) spectroscopy was of "suprapur" grade (Merck).

Synthesis and analysis

The synthesis procedure of the Mn alkoxide, starting with 3g fresh $MnCO_3$ or finely divided MnO_2 was the same as previously reported for iron glycerate (5). The hydrolysis of the glycerol-free Mn-alkoxide was carried out generally on 2g of sample with 400ml boiling water in an open beaker, for one hour. The resulting powder was washed with water, then with acetone and air dried. Total Mn was determined by atomic absorption (AAS) previous dissolution of the solids in HCl. Hygroscopic water was estimated separately by heating in oven at 110°C (until constant weight). Heatings at 275°, 650° and 1000°C were carried out in a calibrated furnace, in air. Qualitative tests for Mn^{3+} and Mn^{2+} in the solids were made both in acid medium, with sodium pyrophosphate and ammonium persulfate (7) respectively. Reactivities were performed upon attack of 50 mg sample with 50 ml 2.5 N HCl for 10 min at 25°C. Then, dissolved Mn was determined by AAS.

Instrumentation

X-ray powder diffractograms (XRD) were taken with a Philips PW 1730 unit using FeK_α radiation at $1°2\Theta$. IR spectra were printed with a FTIR Nicolet spectrophotometer system using 0.25% CsI disks. The CsI salt was slightly ground and dried at 100°C before disking in a vacuum die. The disks were handled and kept in a low humidity ambient. Surface area (BET) was determined in a Quantasorb apparatus using N_2 as adsorbate. Differential thermal analysis (DTA) was performed with a Netzsch equipment on 40 mg sample, from 25 to ~1400°C at a heating rate 10°C min^{-1}, in air.

RESULTS AND DISCUSSION

Synthesis

The transformation of $MnCO_3$ (or Mn oxides) into a hausmanite lattice structure takes place in two steps: 1) reflux with glycerol, resulting in a light brownish solid, identified as Mn alkoxide. A qualitative analysis of this complex reveals the presence of Mn^{2+} and Mn^{3+}. 2) Hydrolysis of the corresponding Mn alkoxide by boiling water yielding a dark brownish powder with the lattice structure of $MnO.Mn_2O_3$. As expected Mn^{2+} and Mn^{3+} are also found in this spinel oxide.

X-ray diffraction

The reaction products obtained after each one of these steps have been examined by XRD. Fig. 1a displays the diffractogram of the Mn-glycerate complex (first step) with the strong characteristic line at 8.36Å. This reflection appears at the same position in Mn alkoxide prepared from Mn acetate (3) or from Mn oxides (like MnO_2 or Mn_2O_3) according to our observations. All the peaks in Fig. 1a correspond to Mn alkoxide indicating a complete transformation of the starting material

Fig. 1b shows a selected (typical) X-ray diffractogram of the powder obtained after the 2nd step, when 2g of Mn alkoxide have been hydrolyzed. The pattern of this material is identical to that

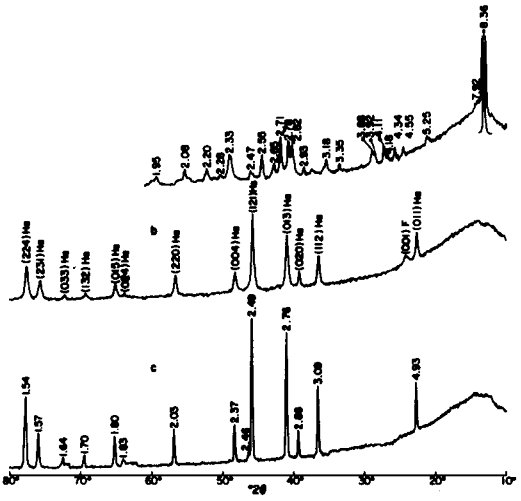

Figure 1. X-ray diffractograms of: (a) Mn alkoxide; (b) sample (a) after hydrolysis; (c) Mn_3O_4 produced by calcination of $MnCO_3$. Ha= Hausmanite; F= Feitknechtite. Spacings in Å.

of hausmanite, Mn_3O_4, except for a small extra reflection at 4.65 Å attributed to the most intense line of Feitknechtite, β-MnOOH. No other crystalline phase is usually detected. For comparison a pattern of reference Mn_3O_4 obtained by calcination in air of $MnCO_3$ at 1000°C is displayed (Fig. 1c). Here the Mn_3O_4 lines appear at the same positions as in 1b but are stronger and sharper, indicating a hausmanite of higher crystallinity. (A small peak at 2.46 Å in Fig. 1c is atypical and appears only in Mn_3O_4 produced by calcination). The X-ray patterns (not shown) of synthetic hausmanite after heating at 275°, 630° and 1000°C reveal a transformation to Mn_2O_3 at 630° and to Mn_3O_4 at 1000°C.

Although the same experimental conditions were carefully observed the amount of β-MnOOH formed in repetitive syntheses was variable. In a few instances only Mn_3O_4 was detected after hydrolysis. The above mentioned variations suggest that the structural rearrangements of the Mn alkoxide after hydrolysis are of a topochemical nature.

Feitknecht and Marti (2) prepared a hydrous compound that had a manganese to oxygen ratio between Mn_3O_4 and MnOOH, by oxidation of an aqueous suspension of $Mn(OH)_2$. The X-ray diffraction pattern of this material revealed also hausmanite, but accompanied by a quite strong reflection of β-MnOOH. This material was named hydrohausmanite, but it was later found to contain a mixture of two phases, β-MnOOH and Mn_3O_4 (8). Unlike in our synthesis, where β-MnOOH is a minor phase, these authors showed that Feiknechtite was a major phase in their preparations. By alkalinization of Mn^{2+} solutions in the presence of oxygen gas Bricker (1) prepared as well a mixture of Mn_3O_4 and MnOOH varieties, the final composition of the material being determined by the oxidation conditions.

IR absorption spectroscopy

Manganese oxide was also synthesized by the method of Mackenzie for birnessite (9) using $MnSO_4$ and KOH, but employing air rather than pure O_2 as the oxidizing agent and acidification of the alkaline material to pH 5 (10). XRD showed the oxide to be Mn_3O_4 although the infrared spectrum revealed sharp absorption bands at 1088, 1120 and 1153 cm^{-1}. The latter bands, not present prior to acidification, were assigned by McBride to structural OH vibrations typical of groutite or manganite (10).

Figure 2a shows a spectrum of our hydrous hausmanite preparation, exhibiting characteristic Mn_3O_4 (Mn-O) absorptions at 428, 520 and

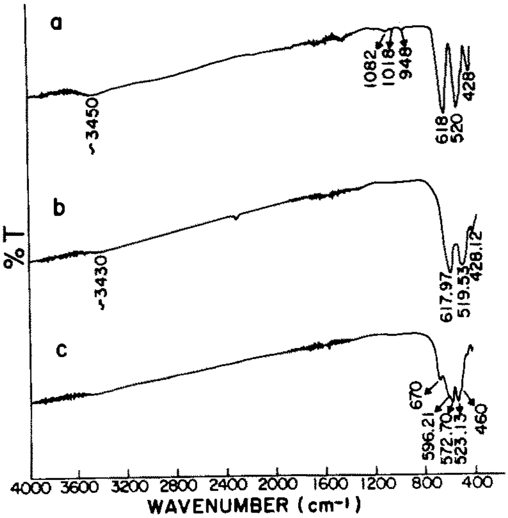

Figure 2. FTIR spectra of: (a) synthetic hausmanite; (b) sample (a) heated at 275°C; (c) sample (a) heated at 650°C

618 cm^{-1}. In addition there is a broad band at 3450 cm^{-1} accompanied by small peaks at about 1082, 1018 and 948 cm^{-1}, indicative of OH groups. It must be pointed out that these OH groups should not be attributed necessarily to the presence of a MnOOH phase, since in these singular instances when our synthesis (2nd step) produces Mn_3O_4 as the only crystalline phase, the OH bands, especially that at 3400 cm^{-1}, appear as well. Thus, an amorphous OH-containing product could also be present in our hausmanite powder. Heating this powder at 275°C causes a decrease in the intensities of the absorption bands (Fig. 2b); at this stage no structural alterations are shown by XRD. Further heating at 650° causes some major changes in the 600-400 cm^{-1} region (Mn-O absorptions) and removes the OH bands (Fig. 1c). This spectrum corresponds to a Mn_2O_3 structure (11), in agreement with the XRD information.

Differential thermal analysis

The curve represented in Fig. 3 is typical of hydrous hausmanite. The formation of β-MnOOH does not change the main pattern. A large endothermic effect at 110°C is due to the loss of non-essential water, the intensity and extension of this effect being variable. The dehydration and dehydroxylation process continues at higher temperatures, until 630°C when Mn_2O_3 is formed, according to the IR and

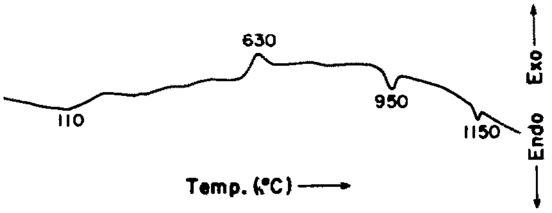

Figure 3. DTA curve of synthetic hydrous hausmanite

XRD information. Thus, the exothermic peak appearing at about 630°C -which is characterized by weight gain- is due to the oxidation of Mn^{2+} to Mn^{3+}. Around 210°C an other exothermic event seems to take place, but it is overshadowed by the ungoing dehydration in the same temperature range. Unfortunately, the equipment conditions did not allow to make runs in other atmospheres, like nitrogen, in order to discern in more detail the dehydration and oxidation processes (12).

Beside the above-mentioned thermal effects, two endothermic peaks are marked in Fig. 3 at 950°and 1150°C. The endothermic event at 950°C is attributed here to the decomposition of Mn_2O_3 to Mn_3O_4, which is consistent with the XRD and IR results of synthetic hausmanite heated at different temperatures. This decomposition is accompanied by a weight loss and has also been reported when Mn_2O_3 (starting material) is heated in air at about 1000°C (13). In contrast, the thermogram of reference (non hydrous) Mn_3O_4 shows only two endothermic peaks at similar temperatures as in synthetic hausmanite. One at about 950°C due exclusively to the tetragonal α to tetragonal β Mn_3O_4 irreversible transition, and another around 1160°C which may be assigned in both hausmanites to the Mn_3O_4 tetragonal to cubic inversion. The latter attributions are based on the excellent review on DTA literature of manganese oxides by MacKenzie (14).

Composition and reactivity

The lack of stoichiometry in manganese oxides and hydroxides due to the different valencies of manganese within one compound is well known (14). Another problem, especially pertinent to our compounds is the variability in the water contents after heating in the lower temperature range (non essential H_2O) as well as at higher temperatures. Bricker (1) came across the same problem in his Mn_3O_4 preparations and could not discern the different forms of HOH. He attributed part of the problem to the finely divided material and its tenacity to hold water. Other factors to consider are the easy oxidation of Mn^{2+} to Mn^{3+} and the transition occurring at high temperatures (around 950°C), both able to alterate the absolute weight variation due to loss of water.

Table 1 gives the formulae calculated from a partial chemical analysis of 6 separate selected syntheses and of reference Mn_3O_4 produced by calcination. Weight losses at 100°C are also given and correspond roughly to the H_2O^- contents in these samples. They were used to correct the Mn contents. The weight losses after heating at 1000°C are between 2 and 20% for the synthetic hausmanite samples.

The variability in chemical composition (see Table) allows us to establish only a general formula having a Mn:O ratio between Mn_3O_4

TABLE 1

Composition, surface area and reactivity of hausmanite samples*

Analyst: R. Villalba

Sample	Formula	Crystalline phases (XRD)	So (m^2g^{-1})	Reactivity (% Mn extracted)	Weight loss at 100°C (%)
H_1	$MnO_{1.61}$	Ha,F	39.4	31.1	11
H_2	$MnO_{1.53}$	Ha,F	42.6	n.d.	2.3
H_3	$MnO_{1.48}$	Ha,F	47.8	31.6	0.7
H_4	$MnO_{1.44}$	Ha,F	38.9	36.3	2.6
H_5	$MnO_{1.43}$	Ha	45.0	31.6	1.4
H_6	$MnO_{1.41}$	Ha	30.7	32.4	1.3
H_7**	$MnO_{1.34}$	Ha	<1	0.7	0

* Prepared indistinctly from $MnCO_3$ or manganese oxides

** Reference Mn_3O_4 produced by calcination of MnO_2 at 1000°C

Ha= Hausmanite; F= Feitknechtite; n.d.= non determined and MnOOH or $Mn(OH)_2$. The eventual formation of a $Mn(OH)_2$ phase is plausible and it could be associated as well with the amorphous product contained in hydrous hausmanite. The presence of this amorphous material may be inferred from comparable investigation by XRD and IR spectroscopy, and from the reactivity and surface area data (Table 1). The latter show that all synthetic hausmanites have almost two orders of magnitude higher surface area than reference Mn_3O_4 produced by calcination. The amorphous material, being finely divided, contributes to this difference in surface area (hence in particle size).

In addition, the reactivities of our hausmanite preparations are considerably higher than reference Mn_3O_4. This may be explained by the finer particle size of the synthetic hausmanite and by the vulnerability of the poorly crystalline phases constituting this non-stoichiometric compound.

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