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REVERSIBLE TOPOTACTIC REDUCTION OF PEROVSKITE-RELATED CALCIUM MANGANESE OXIDES

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ABSTRACT

The perovskite-related solids $CaMnO_3$ resp. Ca_2MnO_4 react upon heating in reducing atmosphere to grossly oxygen-deficient phases: $CaMnO_{2.5}$, $Ca_2MnO_{3.5}$, and $CaMnO_2$, Ca_2MnO_3. Thermogravimetry, X-ray diffraction and electron microscopy reveal the reversible, topotactic nature of the processes important for heterogeneous catalysis.

INTRODUCTION

$CaMnO_3$ and Ca_2MnO_4 represent members of a large group of ternary metal oxides crystallizing in the structure of the naturally occurring mineral perovskite, $CaTiO_3$, resp. the related K_2NiF_4-type.

Whereas structural, magnetic, electric and optical properties of this class of oxides have been investigated extensively (ref.1), their chemical reactivity has not drawn as much attention yet.

For $CaMnO_3$ as well as Ca_2MnO_4 quantitative thermogravimetric measurements proved, that these phases are stable up to 900°C in nitrogen, air or pure oxygen. In hydrogen, ammonia or hydrocarbons such as C_2H_4 and C_3H_6, however, reduction processes take place and grossly oxygen-deficient phases such as $CaMnO_{2.5}$ and $Ca_2MnO_{3.5}$ are formed at relatively low temperatures of 300-350°C (ref.2). By heating these compounds in reducing atmospheres up to 550-600°C, $CaMnO_2$ and Ca_2MnO_3 respectively are formed.

RESULTS AND DISCUSSION

As it can be confirmed by thermogravimetric investigations and by X-ray diffraction, $CaMnO_{2.5}$ and $CaMnO_2$ as well as $Ca_2MnO_{3.5}$ and Ca_2MnO_3 undergo reoxidation at moderate temperatures in order to form the initial phases $CaMnO_3$ and Ca_2MnO_4 again.

Such kind of fully reversible processes are of particular interest in the field of heterogeneous catalysis, since it has been observed by experiments using catalysts containing isotopically labelled oxygen, that bulk-oxygen of the catalyst takes part in selective oxidation processes (ref.3).

In order to check the morphological changes caused by these reduction/reoxidation processes, scanning electron microscopical investigations using single crystalline starting materials, i.e. $CaMnO_3$ and Ca_2MnO_4, were carried out. In Figs. 1-3 the results are presented for the process $Ca_2MnO_4 \rightleftharpoons Ca_2MnO_3$. They clearly show, that the macroscopic shape of the initial single crystal is maintained. The reoxidized product, however, is built up of very small Ca_2MnO_4 crystallites (Fig. 3 b).

The determination of the structural changes during the release of oxygen, i.e. unambiguous information whether phases with randomly or with highly ordered oxygen vacancies and, therefore, with defined structures and stoichiometries are formed, turn out to be difficult:

- The preparation of homogeneous samples with defined stoichiometries affords most accurate quantitative thermogravimetric measurements under well-controlled atmospheres and can only be performed successfully by using microcrystalline initial material.
- The non-stoichiometric phases formed often lack sufficiently large crystalline domains and therefore cannot be identified by conventional structure determination techniques such as X-ray or neutron diffraction.

Preliminary structural and spectroscopic investigations of the phases $CaMnO_{2.5}$ as well as $Ca_2MnO_{3.5}$, however, gave evidence for the change of all $Mn^{+4}O_6$ octahedra in the perovskite-related starting materials into $Mn^{+3}O_5$ square-pyramids in the reduced compounds. The structural framework of the respective precursors, in particular the positions of the metal cations, are preserved (ref.2). The structural reaction mechanism of the reduction and reoxidation is highly topotactic and certainly holds the key for the understanding of the high reversibility.

For the determination of the oxygen vacancy ordering in the phases built up of $Mn^{+4}O_6$ octahedra <u>and</u> $Mn^{+3}O_5$ square-pyramids, i.e. in $CaMnO_{3-x}$ as well as Ca_2MnO_{4-x} (where $0 < x < 0.5$), X-ray and neutron diffraction techniques could not yield satisfactory results. High resolution electron microscopy (HREM) and selected area electron diffraction (SAED) turned out to be most suitable for the structure determinations of the non-stoichiometric intermediates and, moreover, for the elucidation of the topotactic structural re-

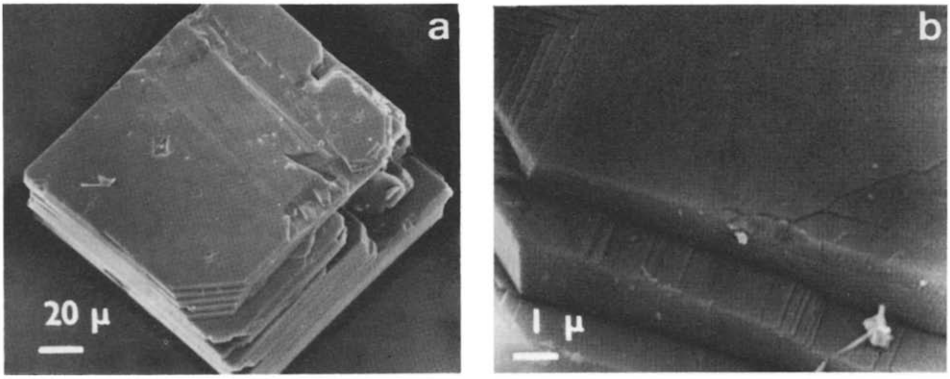

Fig. 1. (a) Ca_2MnO_4 single crystal grown in $CaCl_2$ melt. (b) Surface in detail.

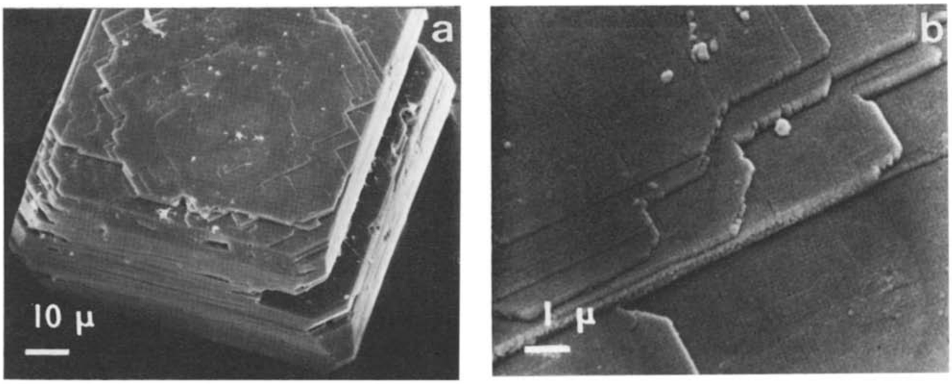

Fig. 2. (a) Ca_2MnO_3 crystal prepared by reduction of single crystalline Ca_2MnO_4 in hydrogen atmosphere (600°C). (b) Surface in detail.

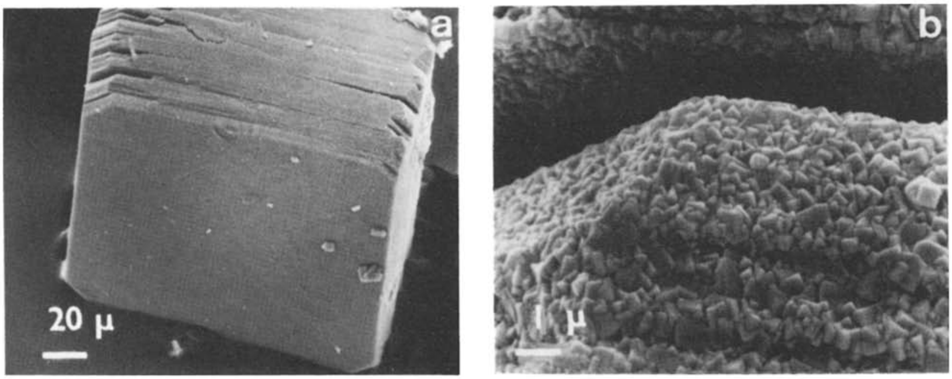

Fig. 3. (a) Ca_2MnO_4 prepared by reoxidation of Ca_2MnO_3. (b) Surface in detail.

action mechanisms. In the case of the reduction process $CaMnO_3 \rightarrow CaMnO_{2.5}$ several intermediates with well-ordered oxygen vacancies and therefore well defined stoichiometries such as $CaMnO_{2.8}$, $CaMnO_{2.75}$ and $CaMnO_{2.667}$ could be identified (refs.4, 5).

The fact that $CaMnO_2$ and Ca_2MnO_3 undergo reoxidation has to be assigned to the formation of extremely small crystallites in the course of the reduction, as it is shown by the morphological investigations (see Figs. 2 a and 2 b for Ca_2MnO_3). Within these compounds the metal cation positions differ from their positions in the respective precursors $CaMnO_{2.5}$ and $Ca_2MnO_{3.5}$, but the diffusion paths, which cations have to undergo during the reoxidation process are very short.

CONCLUSIONS

The reversible reduction processes observed in the compounds $CaMnO_3$ and Ca_2MnO_4 can be summarized as follows:

$$\text{I}: \quad (a) \quad CaMn^{+4}O_3 \rightleftharpoons CaMn^{+4}_{1-2x}Mn^{+3}_{2x}O_{3-x} \rightleftharpoons CaMn^{+3}O_{2.5}$$

$$(b) \quad CaMn^{+3}O_{2.5} \rightleftharpoons CaMn^{+3}_{1-2x}Mn^{+2}_{2x}O_{2.5-x} \rightleftharpoons CaMn^{+2}O_2$$

$$\text{II}: \quad (a) \quad Ca_2Mn^{+4}O_4 \rightleftharpoons Ca_2Mn^{+4}_{1-2x}Mn^{+3}_{2x}O_{4-x} \rightleftharpoons Ca_2Mn^{+3}O_{3.5}$$

$$(b) \quad Ca_2Mn^{+3}O_{3.5} \rightleftharpoons Ca_2Mn^{+3}_{1-2x}Mn^{+2}_{2x}O_{3.5-x} \rightleftharpoons Ca_2Mn^{+2}O_3$$

The fact that the physical and chemical properties of perovskite-related ternary oxides not only depend on the metal cations actually contained but also can be rigorously altered by the formation of the respective oxygen-deficient phases opens up new possibilities for the preparation of materials exhibiting specific properties such as highly selective catalytical activity.

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