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THERMOCHEMICAL REACTIVITY OF MANGANESE(IV) OXIDES IN REDUCING ATMOSPHERE

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Abstract

The thermochemical reduction of a series of structurally and morphologically different natural and synthetic manganese(IV) oxides has been investigated. Measurements have been performed by means of combined thermogravimetry/mass spectrometry, X-ray diffraction and analytical scanning electron microscopy. The mechanisms of the degradation of these materials have been characterized in order to establish standardized procedures for their reactivity as function of structure, morphology and experimental conditions. The corresponding results are the fundament with respect to a reproducible technical application.

Keywords: combined thermogravimetry/mass spectrometry, manganese(IV) oxides, structure and morphology of, thermochemical reduction

Introduction

Manganese(IV) oxides are found in many different modifications. The oxidation state of manganese, however, ranges from +3.4 to +4.0 within these phases. Only in very well ordered pyrolusite, β-MnO_2 as well as in ramsdellite the oxygen stoichiometry reaches 2.0 and all manganese cations adopt the ideal value of +4.0.

Common structural element of all the studied 'manganates' (see below) are the distorted [MnO_6] octahedral which are condensed by corner- or edge-sharing to chain-, tunnel- and layer-type structural frameworks. The stability of the tunnel and layer structures depends on the presence of crystal water and/or cations occupying the interstices of the [MnO_6] octahedral framework. In most of the manganese(IV) oxides elements of disorder are present: Mn(III) instead of

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Mn(IV), Mn(IV) vacancies, protons for charge compensation as well as intergrowths of different phases have to be mentioned as the most important ones [1]. All these phases are commonly denoted as 'manganates' [2]. They are best described by the following formula [3]:

$$Mn^{4+}_{(1-x-y)}\ Mn^{3+}_{y}\ O^{2-}_{(2-4x-y)}\ (OH)_{(4x+y)} \cdot nH_2O$$

Manganates exhibit a rich spectrum of technical applications [4]. The most prominent ones are in battery technology and in heterogeneous catalysis. Especially the last mentioned field of application refers to the high selectivity and activity of manganese(IV) oxides as oxidizing reactants [5]. In many cases, however, the reaction behaviour of these useful manganates is not yet understood. Therefore, the detailed characterization of the manganate phases used is one of the crucial prerequisites for a better understanding of the interrelation between composition, structure, morphology and reactivity of these challenging materials. Moreover and in spite of the many applications of manganates only few research activities have been reported with regard to the elucidation of the key parameters controlling the mechanism of reactions with manganates [6]. In fact, the state of the art in research, development, production and application of manganates is often such – particularly in heterogeneous catalysis – that it rather may be called 'advanced alchemy'. This situation is unsatisfactory because the manganates not only exhibit the mentioned potential as multifunctional materials, but also prove to be very good reversible redox systems and only show low biotoxicity, i.e. a replacement of manganates is very difficult.

For these reasons we started to examine composition, structure, morphology and reactivity of various, technically used manganates [7]. Owing to the comparatively extensive knowledge of manganate-gas-reactions in inert or oxidizing atmospheres we decided to perform reactions with hydrogen as standard for the characterization of the reactivity.

Experimental

Thirteen different manganates have been investigated by means of thermal analysis combined with simultaneously working mass spectrometry (NETZSCH STA 409C connected by a heated capillary/gas inlet system to a BALZERS QMG 421 mass spectrometer). The samples were placed in alumina crucibles, exposed to a flowing mixture (50 ml min^{-1}) of 5% H_2/95% N_2 and heated with a rate of 10 up to 1000 or 1300°C.

Results

Structural features and thermochemical reactivity

Well ordered manganates like pyrolusite, β-MnO_2 show the highest onset temperature for the reduction process (Fig. 1). This is also observed for the merely thermal reduction. The onset temperatures of manganates adopting tunnel structures such as α-MnO_2 with a 2×2-tunnel (Fig. 2) is lowered by ~50^oC. In Fig. 3, the structure and the thermochemical reduction of γ-MnO_2 is presented. The structural framework may be described as an intergrowth of the two well ordered phases pyrolusite and ramsdellite containing many structural and compositional defects. The onset temperature is slightly lower than the one of α-MnO_2. Finally, δ-MnO_2, birnessite, adopts a layered structure (Fig. 4). The onset temperature is registered at very low temperatures, i.e. around 200^oC.

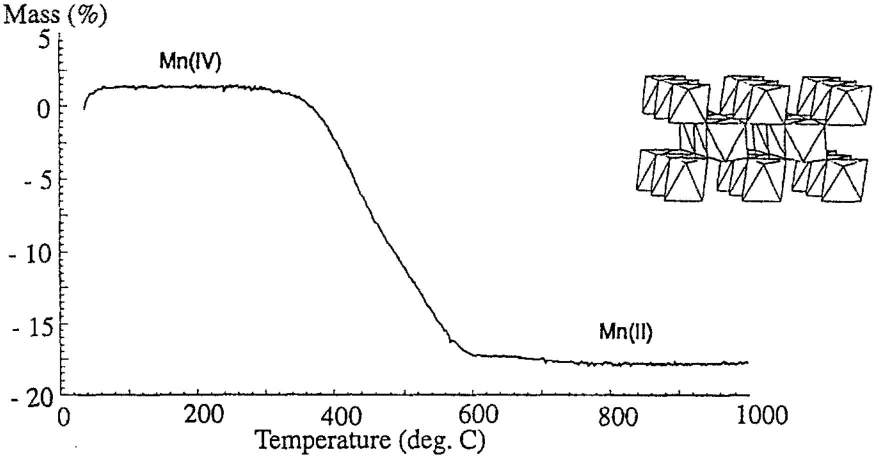

Fig. 1 Structural framework and TG measurement of the thermochemical reduction of pyrolusite, β-MnO_2 in a 5% H_2/95% N_2 atmosphere (temperature range: 50 to 1000°C; heating rate: 10°C min^{-1})

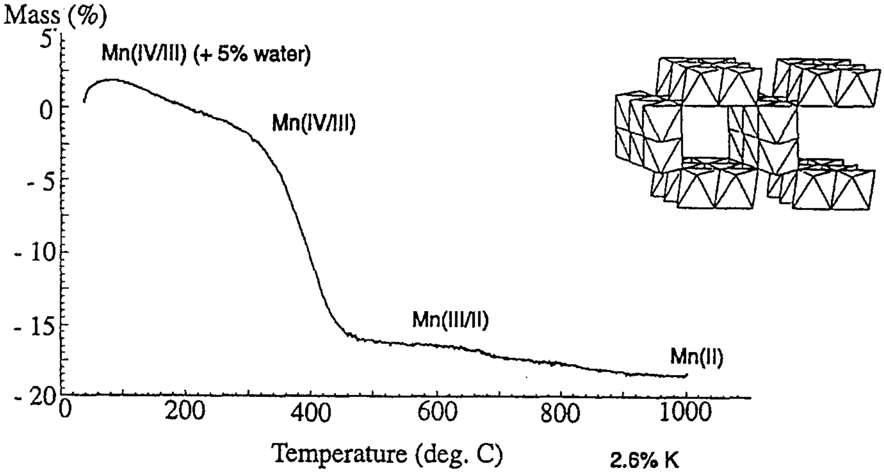

Fig. 2 Structural framework and TG measurement of the thermochemical reduction of α-MnO_2 in a 5% H_2/95% N_2 atmosphere (temperature range: 50 to 1000°C; heating rate: 10°C min^{-1})

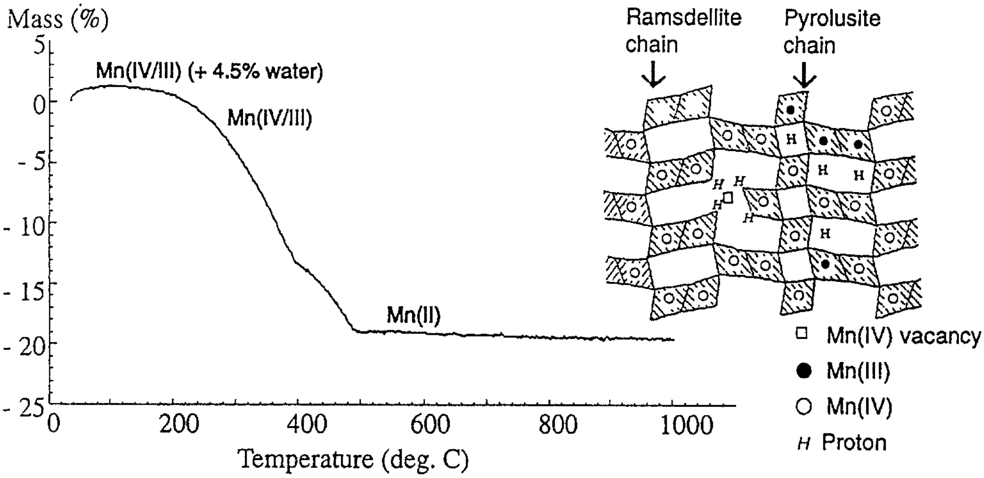

Fig. 3 Structural framework and TG measurement of the thermochemical reduction of γ-MnO_2 in a 5% H_2/95% N_2 atmosphere (temperature range: 50 to 1000°C; heating rate: 10°C min^{-1})

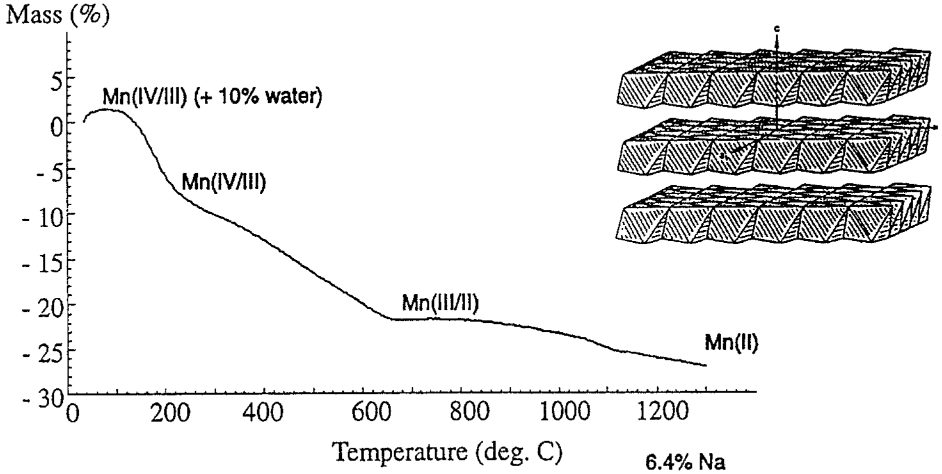

Fig. 4 Structural framework and TG measurement of the thermochemical reduction of δ-MnO_2 in a 5% H_2/95% N_2 atmosphere (temperature range: 50 to 1000°C; heating rate: 10°C min^{-1})

Effects caused by the morphology and the particle size

Previous investigations have shown that the reduction of manganese(IV) oxides by hydrogen strongly depends on the diffusion rates of hydrogen and water within the reacting solid [10]. During the reduction, manganese oxides contain-

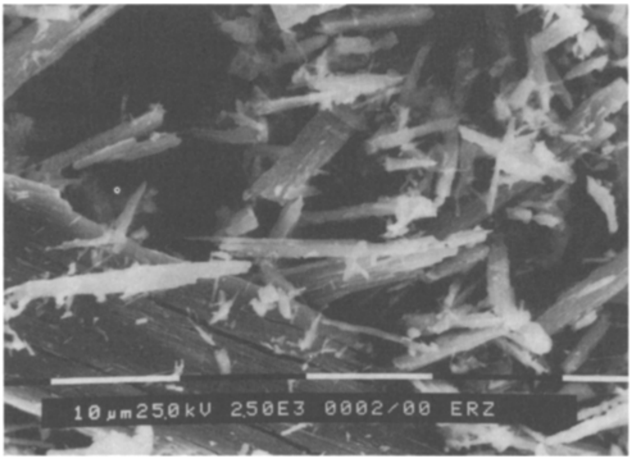

Fig. 5 Scanning electron micrograph of a manganate showing the end of the first mass loss in a 5% H_2/95% N_2 atmosphere at 680°C

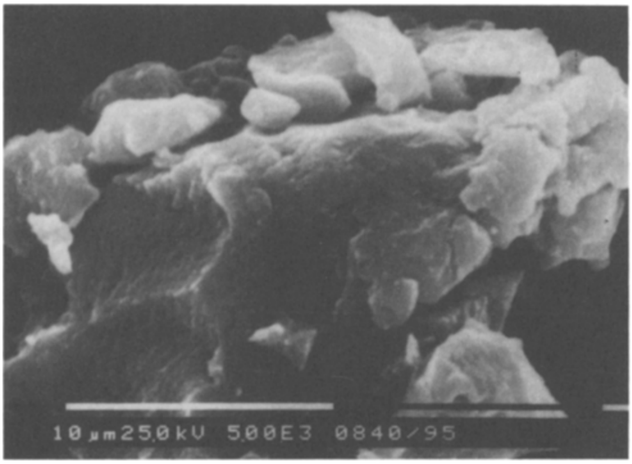

Fig. 6 Scanning electron micrograph of a manganate showing the end of the first mass loss in a 5% H_2/95% N_2 atmosphere at 680°C

ing manganese cations with low oxidation states are formed on the particle surface and retard the process. As complementary studies by thermal analysis, X-ray and scanning electron microscopy (Figs 5–8) prove, the particle size and even the morphology of the particles decide upon the reactivity.

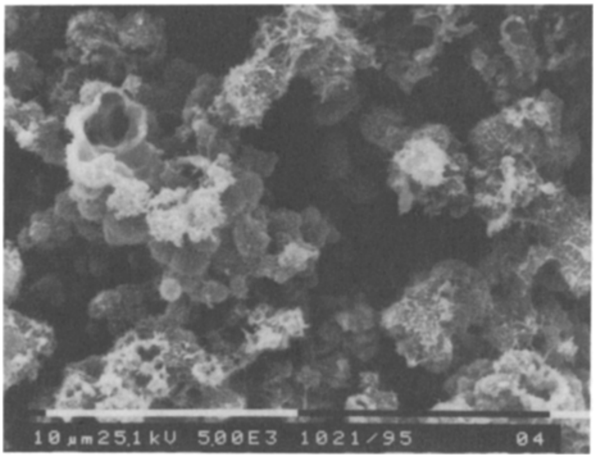

Fig. 7 Scanning electron micrograph of a manganate showing the end of the first mass loss in a 5% H_2/95% N_2 atmosphere at 420°C

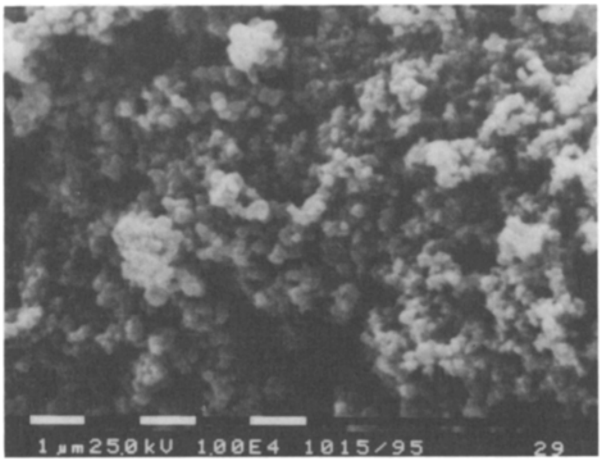

Fig. 8 Scanning electron micrograph of a manganate showing the end of the first mass loss in a 5% H_2/95% N_2 atmosphere at 460°C

The role of the manganese content

Manganates with a high manganese content (>55%) exhibit high onset temperatures for the reduction (Fig. 9). However, the course of the reduction is characterized by a high velocity compared to phases with lower manganese con-

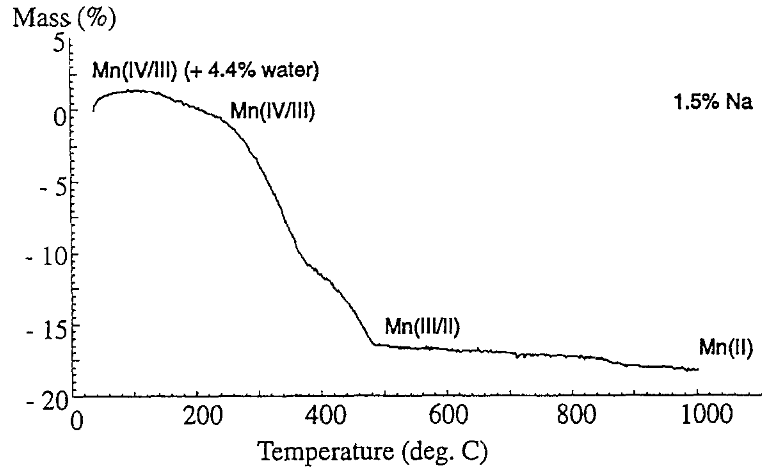

Fig. 9 TG measurement of the thermochemical reduction of a technical manganate containing 57.1% manganese in a 5% H_2/95% N_2 atmosphere (temperature range: 50 to 1000°C; heating rate: 10°C min^{-1})

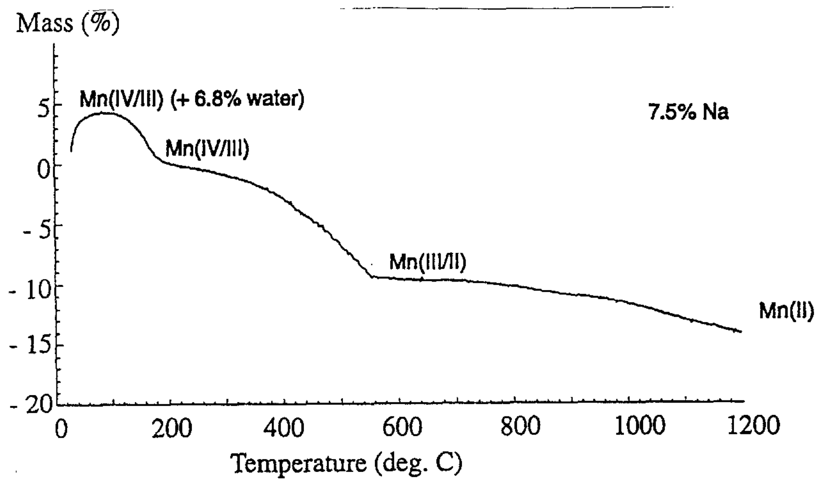

Fig. 10 TG measurement of the thermochemical reduction of a technical manganate containing 44.6% manganese in a 5% H_2/95% N_2 atmosphere (temperature range: 50 to 1000°C; heating rate: 10°C min^{-1})

tents. This finding can be explained by the comparison with the reactivity of phases containing ~45% manganese. Such materials also contain alkali ions and usually adopt a poorly ordered structure. Their reduction starts at low temperatures, i.e. <200°C (Fig. 10). But the course of the reduction spans over a large temperature range. A second mass loss is usually registered at temperatures >700°C. It can be explained by the segregation of e.g. $KMnO_2$ into K_2O and MnO.

The role of alkali metals on the reduction mechanism

Manganates containing no alkali ions undergo reduction in a single-step process (see e.g. Fig. 1). Alkali contents lead to a mass loss at temperatures >700°C (Figs 11 and 12). As mentioned above this mass loss can be explained by the segregation of ternary alkali manganates, where manganese still adopts the formal oxidation state +III [11]. Accordingly, the size of this second mass

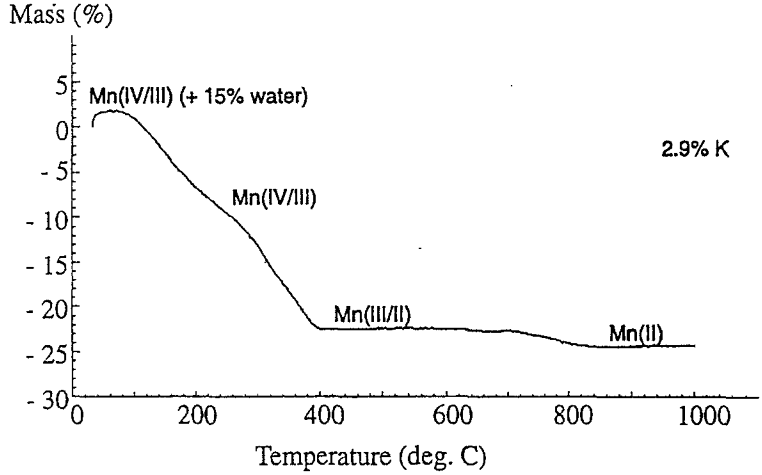

Fig. 11 TG measurement of the thermochemical reduction of a technical manganate containing 2.9% potassium in a 5% H_2/95% N_2 atmosphere (temperature range: 50 to 1300°C; heating rate: 10°C min^{-1})

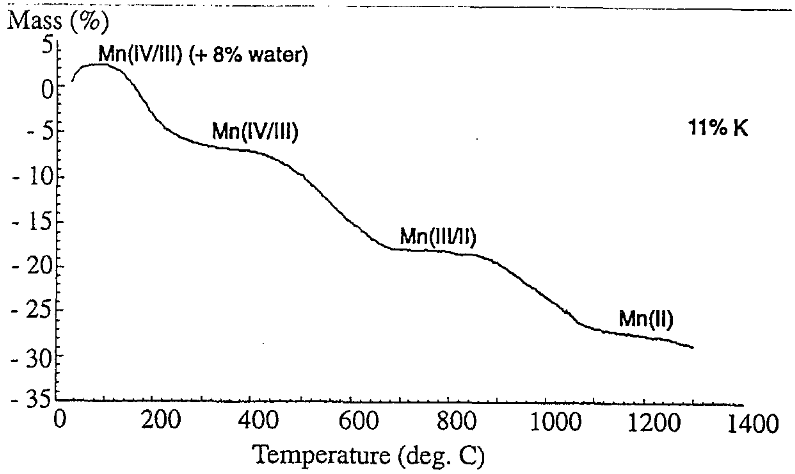

Fig. 12 TG measurement of the thermochemical reduction of a technical manganate containing 11% potassium in a 5% H_2/95% N_2 atmosphere (temperature range: 50 to 1300°C; heating rate: 10°C min^{-1})

loss at high temperatures depends on the alkali content of the parent manganate. Phases containing large amounts of alkali ions decompose by evolution of K_2O/Na_2O above 1100°C (Fig. 12). This leads to a larger overall weight loss than expected for the complete reduction to manganese(II) oxide and the alkali metal oxides.

Conclusions

The presented experimental findings reveal that the following key parameters decide upon the thermochemical reactivity of manganates:

- manganese and alkali ion content
- particle size and particle morphology
- defect structure and texture, i.e. the 'Realstruktur'

The water content is not decisive because the diffusion rates are rather high at the given experimental conditions. This may be drastically changing when reactions are carried out in e.g. non-polar fluids or solvents. The oxidation state of manganese only contributes to the total mass loss of the reduction. A direct correlation between oxidation state and shifts of onset and end temperatures is not observed.

The use of small particles with a large surface seems to be crucial for a high reactivity. This can be explained by the decisive role of the diffusion processes taking place during this type of heterogeneous solid state reactions. Working with nano- or microparticles also reduces the disadvantageous effects of manganese oxide products covering the surfaces of the reacting particles and hindering the contact of the reactants.

Manganates containing alkali ions and adopting many structural defects undergo reduction at lower temperatures than highly ordered, manganese rich phases. In technical terms, the former prove to be very active. But the reduction of these alkali containing manganates is incomplete, except under drastic conditions. Consequently, they have to be used in excess in order to reach equivalent turn-over rates. In turn, these alkali manganates may easily undergo reoxidation and thus may be used as recyclable oxidants.

Perspectives

Forthcoming activities include the standardization of the thermochemical reactivity of manganates by the reaction with hydrogen. The manganate structures and textures involved will be studied in detail by electron diffraction and high resolution electron microscopy techniques. Based on the present knowledge synthesis pathways are designed which lead to manganates exhibiting reproducible reactivity. This approach is decisive for a successfull implementation into technical processes. Finally, the reactivity of manganates will be tested as oxidants for organic compounds and the reversibility of reduction/reoxidation cycles will be studied.

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