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INTERNAL AND EXTERNAL PARAMETERS DETERMINING PROPERTIES AND REACTIVITY OF SOLIDS

A. RELLER

Anorganisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich (Schweiz)

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ABSTRACT

Investigations on heterogeneous solid-state reactions comprising compositional, structural and morphological changes as well as concomitant alterations of the physical properties are presented. Owing to the fact that mere thermoanalytical techniques yield only limited results, independent complementary methods of investigations, such as X-ray diffractometry, light and electron microscopy, as well as spectroscopic techniques are applied in order to achieve a consistent interpretation of the course of the processes investigated, as well as of the properties of the products formed. Due attention is paid to the role of inert or reactive gas atmospheres. The reactions studied comprise thermal degradations of pure and mixed alkaline-earth/transition metal carbonates in various gas atmospheres as well as thermal reduction/reoxidation processes of perovskite-type and delafossite-type metal oxides. The importance of the investigated compounds in the field of heterogeneous catalysis and of materials with specific magnetic or electronic properties, such as semi- or super-conductors, is discussed.

INTRODUCTION

The chemistry and physics of solids not only represent topics of pure scientific interest, but are of increasing importance in the field of applied sciences as well as materials research and development [1]. The controlled preparation of solids with specific physical properties by homogeneous or heterogeneous solid state reactions, in fact, as well as the understanding of the chemical reactivity of solid materials are of widespread interest.

Thermoanalytical techniques prove to be appropriate tools for a better

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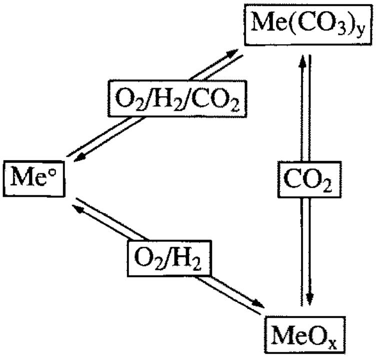
understanding of the reactivity of solids, inasmuch as they provide quantitative data on temperature- and/or time-dependent changes of the compositional and thermodynamic properties that represent important internal parameters specifying any solid material [2]. Moreover, the influence of external parameters, above all of the actual gas atmosphere as an inert or reactive medium, can also be investigated quantitatively by thermal analysis.

Assessment of the influence of the structure and the morphology of a solid on the course of temperature-induced processes, as well as the characterization of concomitant changes of physical properties, however, requires information obtainable by independent complementary methods of investigation, such as X-ray diffractometry, light and electron microscopy, spectroscopical techniques, measurements of conductivity and magnetism, etc. [3,4].

The relevance of this statement will be illustrated by studies on heterogeneous processes comprising metals and/or alloys, pure and/or mixed metal oxides, as well as binary and/or ternary metal oxides as the solid parent or product phases. Measurements were carried out under inert or reactive gas atmospheres. As main volatile reagents, hydrogen, oxygen and carbon dioxide were used, and during some of the investigated decompositions, they also were formed (O_2 and CO_2). The following scheme shows that the conversions investigated are mutually interrelated. It represents a closed cyclic system made up of reversible processes.



The reason for studying well known processes, such as the displayed decarbonatization/recarbonatization of metal carbonates/metal oxides, as well as the reduction/reoxidation of metal oxides/elemental metals lies in the fact that through the best possible selection and control of these internal and external parameters, not only new synthetic pathways are found, but products with specific properties are materialised.

THE THERMAL REACTIVITY OF PURE AND DOPED ALKALINE-EARTH METAL CARBONATES IN A REDUCING ATMOSPHERE

Metal carbonates are among the most abundant minerals in the earth's mantle. They were and still are formed as precipitates by the reaction of atmospheric carbon dioxide with dissolved metal ions, or as deposits by the carbonatization of metal oxides, metal hydroxides or further naturally occurring metal compounds. The thermal degradation of these compounds has been studied *in extenso*. Among the most important findings, these investigations revealed that the ambient gas atmosphere influences not only the temperature range, but also the kinetics of decomposition of parent carbonates [5]. The most pronounced effects originate from the partial pressure of carbon dioxide, especially in the decomposition of calcite [6].

Quite surprisingly, there are only a few studies on the thermal degradation of metal carbonates in reducing atmospheres. We therefore set out to study the thermal behaviour of the most abundant natural metal carbonates, magnesite $MgCO_3$, dolomite $MgCa(CO_3)_2$ and calcite $CaCO_3$, in molecular hydrogen by simultaneous thermogravimetric/mass spectrometric techniques [7,8]. As our first result, we found that the reaction onsets are shifted towards remarkably low temperatures. Compared with the analogous processes in inert atmospheres, the lowering is in the range of 150 K for the decomposition of calcite in argon respectively hydrogen [7]. For the experiments carried out in a reducing atmosphere, mass spectrometric investigations of the evolved gases prove the formation of considerable amounts of carbon monoxide. Thus, during the course of decarbonatization, reduction of the C(+IV) of CO_2 occurs. Electron microscopy reveals that the solid products, i.e. the alkaline earth metal oxides, are formed as small particles with dimensions well below 1µm. Particles with comparable dimensions are obtained by the decomposition of these carbonates under reduced pressure.

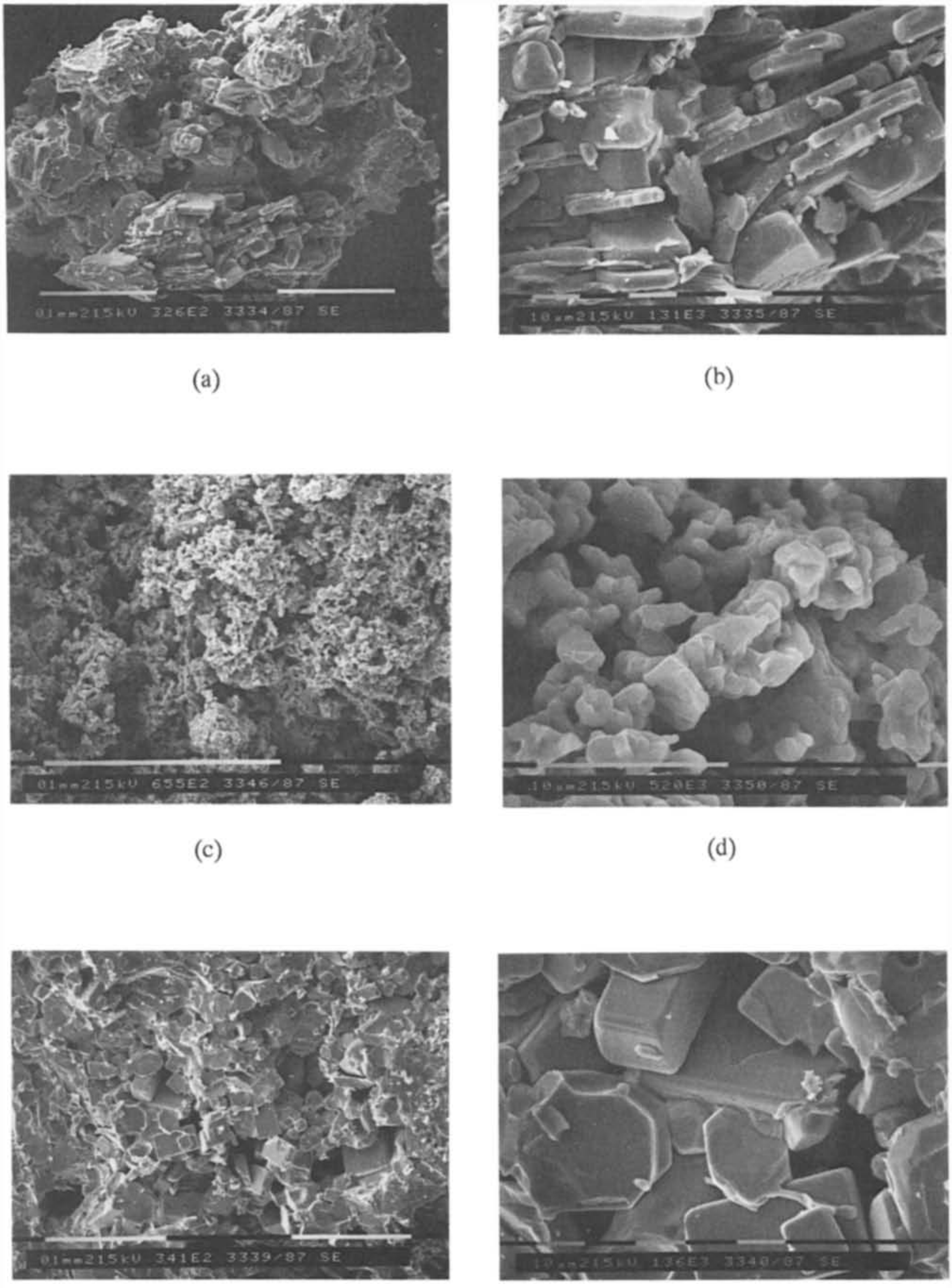
Recent studies on the recarbonatization of such metal oxides, in particular of microcrystalline calcia, have shown that at low temperatures amorphous calcium carbonate is formed. By heating this material, recrystallization is observed by differential thermal analysis, as well as by temperature-dependent X-ray diffractometry [9]. These results offer a good explanation on the fact that microcrystalline calcia can be used as an efficient carbon dioxide trapping compound.

The effect of transition metal dopants on the course of the decarbonatization of alkaline earth metal carbonates in a reducing atmosphere, i.e. in molecular hydrogen (10^5 Pa), has been studied by inserting copper, cobalt and nickel in the parent calcium carbonates [8]. For all mixed phases, a remarkable decrease of the decomposition temperatures is observed. This decrease ranges between ~150 K (for the Cu/Ca system and ~400 K (for the Ni/Ca system). As combined TG/MS measurements prove, the kind of volatile carbon compound evolved directly depends on the transition metal present. For copper doped calcium carbonate, carbon monoxide is formed as main product (>90%). For cobalt doped calcium carbonate, carbon monoxide and methane are detected. In the case of nickel doped calcium carbonate, methane is the main volatile carbon compound (>90%). In conclusion, the combination of heterogeneous-solid state reactions with catalyzed molecular conversions allows the production of an organic carbon compound, i.e. methane, from an inorganic metal carbonate. Prerequisites are the use of parent materials characterized by specific internal parameters, i.e. compositional features, as well as the performance of processes under well-controlled external parameters, i.e. molecular hydrogen as reactive gas.

PREPARATION AND REACTIVITY OF PEROVSKITE-TYPE AND DELAFOSSITE-TYPE METAL OXIDES

Coprecipitated metal carbonates are well-suited precursor phases for the synthesis of mixed metal oxides. Depending on the composition of the parent carbonates, i.e. the actual metal combinations as well as the actual ratio of the metals, ternary or quaternary metal oxides adopting respective structures, namely spinel AB_2O_4, perovskite ABO_3 or delafossite ABO_2 and others, are obtained. Thermoanalytical techniques are well suited for the monitoring of such calcination processes and thus the elucidation of the kinetic and mechanistic course of the formation of these metal oxides from precursor compounds.

In Fig. 1, scanning electron micrographs of $YBa_2Cu_3O_{7-x}$ samples are presented. In order to investigate the influence of the composition of the precursor material on the course of the calcination, as well as on the properties of this recently discovered perovskite related ceramic superconductor [10], mixed carbonates, formates and oxalates were calcined under analogous experimental conditions. As the micrographs prove, the different internal parameters of the parent precursors lead to different morphological properties of the products formed. This can be attributed to differences in the precursor decomposition mechanisms and to influences of the self-generated atmospheres. Experiments under CO_2 gave evidence for an increased sintering, an effect which is known from the thermal reactivity of pure metal carbonates as well



(a) (b)

(c) (d)

(e) (f)

Fig. 1. Scanning electron micrographs of $YBaCu_3O_{7-x}$ samples prepared by calcination of three precursor systems: (a) and (b) from mixed Y/Ba/Cu-carbonates; (c) and (d) from mixed Y/Ba/Cu-formates; (e) and (f) from mixed Y/Ba/Cu-oxalates.

(see e.g. [11]). Analogous phenomena are observed for perovskitic or spinel-type products obtained by this preparative method. As the formation of $YBa_2Cu_3O_{7-x}$ proves, phases containing metals with unusual formal oxidation states (partly Cu^{3+}) can be stabilized.

In oxidizing or inert gas atmospheres, ternary or quaternary metal oxides prove to be stable up to high temperatures. In the case of rare earth superconducting ceramics such as $YBaCu_3O_{7-x}$ thermogravimetric measurements reveal thermally induced reversible reduction/reoxidation processes (see Fig. 2). Concomitantly, the (formal) oxidation state of Cu is changed. The perovskitic structural framework, however, is conserved within the range between $YBaCu_3O_7$ and $YBaCu_3O_6$ (see also [12]).

In effect the superconducting properties strongly depend on the oxygen stoichiometry and therefore on the (formal) oxidation state of Cu. Thus, thermally induced reversible reduction/reoxidation results in both the alteration of the crystallographic and the electronic structure, i.e. the physical properties. The kinetics of these reduction/reoxidation processes plays an important role with respect to the controlled production of maximally oxidized phases, i.e. the physical properties depend on the internal parameters and can be changed by the thermoanalytically controlled external parameters, such as heat and atmosphere. Moreover, the kinetic course of these redox processes is strongly dependent on the morphology and size of the present crystallites. Thus, the possibility of controlling the morphological features of the product phases by appropriate selection of the precursor materials is of paramount importance.

This fact reflects a remarkable property of perovskite-related metal oxides: oxygen vacancies can be accommodated without formation of e.g. shear structures or total collapse of the structural framework. The formation of related oxygen-deficient perovskitic structures has been observed by partial reduction of transition metal perovskites such as $CaMnO_3$, $LaCoO_3$, etc. (see e.g. [13]). Whereas the pure perovskites ABO_3 are made up of a three-dimensional network of corner-sharing BO_6 octahedra and of A cations occupying the interstices between them, the oxygen-deficient phases adopt ordered structures made up of BO_6 octahedra combined with BO_5 square-pyramids (Cu and Co perovskites), BO_4 squares (Ni perovskites) or BO_4 tetrahedra (Fe and Co perovskites). The position of the metal cations, however, are conserved, a fact which satisfactorily accounts for the reversibility of the reduction/reoxidation processes. The actual structural reduction mechanism leading to such ordered structures is obviously governed by the present transition metals, i.e. the B cations.

In general, the reactivity of perovskite-type metal oxides strongly depends on

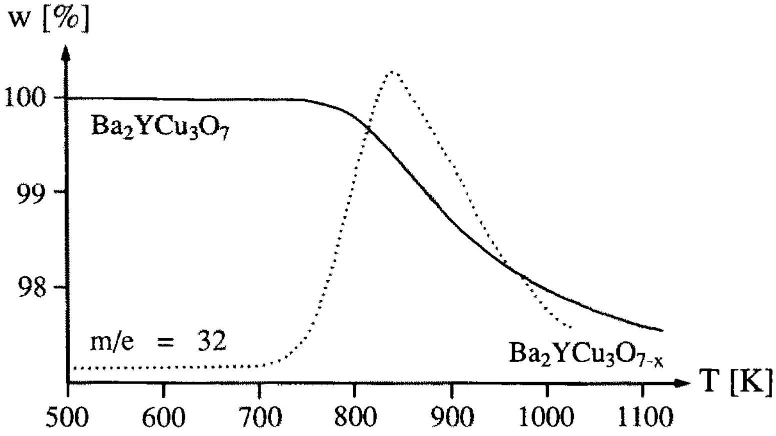


Fig. 2. Thermogravimetric and simultaneous mass spectrometric measurement of the thermally induced reduction of $YBa_2Cu_3O_7$. (atmosphere: N_2; heating rate: 20 K min^{-1}; m/e=32:O_2).

their internal parameters, i.e. the metal present: whereas phases containing Fe, Co, Mn, Ni or Cu in the B position easily undergo reduction, phases such as $SrTiO_3$ cannot be reduced in molecular hydrogen. In turn, perovskites containing precious metals in the B position are reduced at temperatures below 500 K. The products are mixtures made up of microcrystals of the elemental precious metal (size of the domains<10 nm) and the oxide of the A cation.

In conclusion, the thermal behaviour of perovskite-type metal oxides directly depends on the composition and on the atmosphere. Reversible metal-selective reduction/reoxidation processes are observed and oxygen-deficient, ordered structures of phases in the range of ABO_3 to ABO_2 can be synthesized. This reactive behaviour explains the fact that perovskitic metal oxides are potential catalysts [14]. Moreover, the possibility of stabilizing or changing the oxidation states of the metals occupying the B positions without destroying the main structural features allows fine-tuning of the physical properties of these materials. This fact is further supported by the possibility of stabilizing a great number of metal combinations within the perovskite structure. Access to these interesting phases, however, is only guaranteed by careful control of the experimental conditions during their preparation by thermoanalytical techniques as well as detailed characterization of the properties of the products obtained by structural, morphological, chemical and physical methods of investigation.

By changing the metal combinations in the precursor materials, delafossite-type metal oxides A(+I)B(+III)O_2 can be obtained. As observed in the class of perovskitic metal oxides, a remarkable number of different metal cations are accommodated in the A respectively B positions of the delafossite structure. Moreover, compounds of the type $A_{(1-x)}A'_xBO_2$ respectively $AB_{(1-y)}B'_yO_2$ can be prepared as crystalline phases with homogeneous distributions of the metal cations [15,16]. Delafossites adopt a highly anisotropic, layered structure which is made up of linearly coordinated A(I) cations interlinking sheets of edge-sharing $B(III)_6$ octahedra (see e.g. [17-19]). In general, the thermal behaviour of these metal oxides directly depends on the metal present. In oxidizing or inert gas atmospheres, they prove to be stable up to>1000 K. In reducing atmosphere, i.e. in molecular hydrogen, decomposition is observed. The onset temperatures of these reduction processes range between 450 K (for e.g. $CuRhO_2$) and 1050 K for e.g. $CuAlO_2$) [20,21]. In contrast to the formation of highly oxygen-deficient phases as determined for the reduction of certain transition metal perovskites, the kinds of reduction products of delafossites are directly dependent on the composition of the parent phases. As characterized by thermogravimetric measurements, temperature-dependent X-ray diffractometry and high resolution electron microscopy, solid products made up of either mixtures of elemental metals and metals oxides (e.g. Cu° and Al_2O_3 from $CuAlO_2$), of metastable alloys (e.g. CuRh from $CuRhO_2$) or of mixtures of elemental metals, alloys and metal oxides (Cu°, CuRh and Al_2O_3 from $CuRh_{(1-y)}Al_yO_2$) are obtained. Such products are not only of interest with respect to the preparation of metastable metallic compounds, but also represent bimetallic catalysts supported on alumina [22].

CONCLUSIONS

The studies presented are aimed at illustrating the complexity and concomitantly the potential of the characterization of the reactivity and the properties of solids by paying due attention to the determination of internal and external parameters. Although a comprehensive theory describing the chemistry and physics of solid phases is far from being established, the totality of the experimental results often allow preparation or alteration of materials exhibiting 'tailor-made' properties. The requirement for additional fundamental studies, however, is obvious. This means that, apart from the purposeful development of solids with technically important properties, both, model substances and processes must be further investigated on a purely scientific basis. In both fields, thermal analysis plays an irreplaceable role. The respective information provided, however, will only attain its appropriate value if it is integrated in a framework of complementary experimental methods of investigation.

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