# Synthesis and real structure of inorganic materials

Hans-Rudolf Oswald and Armin Reller

Institute for Inorganic Chemistry, University of Zürich,
Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

ABSTRACT - The generation of new or known inorganic compounds with specific chemical and physical properties is discussed. Inorganic solid state chemistry comprising the interrelated topics *'Reactivity of Solids'* and *'Heterogeneous Solid State Reactions'* gets most relevant. As a consequence processes of the type

$$\Sigma \text{ Solids I} + \Sigma \text{ Gases I} \quad \rightleftarrows \quad \Sigma \text{ Solids II} + \Sigma \text{ Gases II}$$
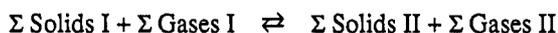
need to be studied with respect to an optimization of the experimental conditions under which the desired products are obtained. Thus, not only the selection of appropriate parent solids, but also the knowledge of the role of the volatile agents are considered as indispensable prerequisites. Moreover, it is necessary to pay due attention to topochemical aspects, and to emphasize detailed investigations on structural relationships between the solids involved, i.e. *'Topotaxy'*. Influences of the actual reactive or inert gas atmosphere as well as the actual pressure on the course of reaction and thus on the product formation are used for the generation of materials with specific properties. Finally, features of the *'Real Structure'* of the so-formed mono- or multiphasic materials, comprising morphology, size of particles, domain structures, etc., are described.

Quantitative thermal analysis combined with independent complementary techniques such as X-ray diffraction, light and electron microscopy, simultaneous mass spectrometry or gas chromatography, etc., prove to represent well-suited tools for such studies. The determination of kinetic data is conducive in order to get further insights into the fundamental problem of establishing correlations between *macroscopic* and *microscopic reaction mechanism*.

As illustrative examples the controlled generation of microcrystalline materials from suitable precursor phases such as mixed metal carbonates, oxides or coordination compounds are described. The products — catalytically relevant dispersed metals or alloys on oxidic supports, mono- or biphasic transition metal sulfides, etc. — represent members of a framework which constitutes the basis for the generation of *'tailor-made inorganic materials'*.

INTRODUCTION

The synthesis of solids and the description of their compositional, structural and morphological features, the knowledge of the principle of their chemical bonding as well as the characterization of their physical properties are representing a major part of solid state chemistry. These days, the development of new as well as the reproducible preparation of known inorganic compounds with specific chemical and physical properties are of increasing importance. This situation reflects mainly demands evoked by the actual significance of materials science and technology, as pointed out in e.g. (ref. 1).

Apart from interests in the abovementioned intrinsic properties of solids, the investigation of their modification as a function of external parameters such as temperature, pressure, surrounding medium (atmosphere), i.e. research in the field of *'Reactivity of Solids'*, is indispensable. Consequently, detailed kinetic and mechanistic studies of *'Heterogeneous Solid State Reactions'* are necessary. They aim in establishing correlations between processes occurring on a microscopical, even on the atomic level, and simultaneously induced changes on a macroscopic level. This allows to derive conclusions, which define mutual dependences and interactions, and which yield in principle quantitative and qualitative data on the reactive behaviour of a *'real solid'*.

Moreover, they constitute the experimental and theoretical basis to control and therefore directly influence such heterogeneous processes. Thus, appropriate pathways for the generation of products are opened, which can be optimally applied as e.g. heterogeneous catalysts.

The heterogeneous solid state processes, on which this contribution as well as previous work (see e.g. refs. 2,3) focus, are mainly of the type

$$\Sigma \text{ Solids I} + \Sigma \text{ Gases I} \quad \rightleftharpoons \quad \Sigma \text{ Solids II} + \Sigma \text{ Gases II}$$
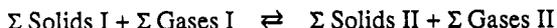
Structural and morphological features of all solid compounds being involved in this type of reactions decisively influence the mechanism and the kinetics. As a consequence of the *complex nature of real solids* comprising all their various properties, the knowledge of their *actual form* must be considered as integrated characteristics of any interpretation. Solids react as *individuals*. Their reactive behaviour towards 'partners' proves to be accordingly manifold and differentiated. Specific properties constituting the individuality of solids comprise:

- size and shape of particles
- texture of materials
- crystallographic planes making up the surfaces
- mutual orientation relationships of individual particles in bi- or multiphasic materials.

Concentration on the changes of merely structural features during the course of solid state reactions, i.e. phenomenological studies on crystallographic orientation relationships between parent solid, eventual intermediate, and product phases (topotaxy) leads to the elucidation of *structural reaction mechanisms* (refs. 4,5). Together with the selection of suitable initial phases, i.e. precursors, the knowledge of such mechanisms enables the control of the product properties. As a matter of fact, there are solids which can only be obtained from topotactic processes.

The actual reactive or inert gas atmosphere as well as the actual pressure conditions can be used to influence the course of a heterogeneous conversion in a decisive way.

Quantitative thermal analysis combined with independent complementary techniques such as X-ray diffraction, light and electron microscopy, simultaneous mass spectrometry or gas chromatography, etc., represents the well-suited tool for such studies (ref. 6). Moreover, energetic and kinetic data can be evaluated from thermoanalytical measurements. Thus, insights into the fundamental problem of establishing correlations between microscopic and macroscopic reaction mechanisms can be achieved.
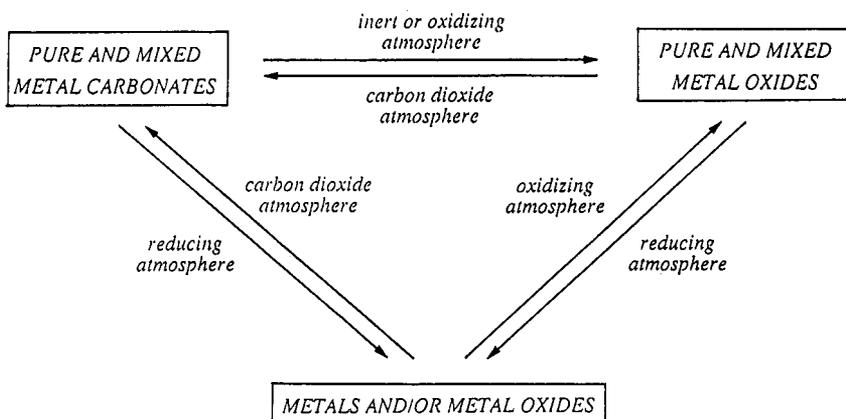
Based on this approach, the aim of the present work is focussed on the controlled generation of microcrystalline solid materials by thermally degrading suitable precursor phases such as pure or mixed metal carbonates, pure and mixed metal oxides as well as inorganic complexes. The desired products, e.g. catalytically relevant dispersed metals or alloys on appropriate supports, metal oxides, mono- or biphasic transition metal sulfides, are often metastable or they tend to undergo sintering or phase segregations at elevated temperatures. Thus the careful selection of the parent materials is the fundament for the production of interesting phases at relatively low temperatures. The following examples are thought to be members of a conceptional framework, which constitutes the basis for the generation of 'tailor-made inorganic solids'.

MATERIALS GENERATED FROM METAL CARBONATES AND METAL OXIDES

The topics depicted in this chapter comprise the thermal reactivity of of metal carbonates and metal oxides. As it is shown in Scheme I, the studied processes are embedded within a framework of interrelated conversions, which can be directly controlled by the selection of the actual atmospheres and by the actual thermal treatment. Moreover, this scheme aims in demonstrating the potential of so-called conventional heterogeneous solid state reactions: Depending on the requested products, e.g. metallic phases, metal oxides, metal carbonates or mutual mixtures of two or more of these compounds, appropriate synthetic routes can be found. The partly reversible course of the said reactions proves to be a useful tool, especially for the generation of solids with specific morphological and textural properties.

The knowledge of the thermal reactivity of pure or mixed metal carbonates is necessary for their use as parent materials for the generation of inorganic solids with specific compositional, structural and morphological properties. Thus, mixed earth alkali/transition metal carbonates are well known precursor systems for the generation of ternary or quaternary metal oxides such as spinels, perovskites, etc. The course of such syntheses strongly depends on the experimental conditions, under which the precursor systems have been prepared as well as thermally treated.

Scheme 1

```
┌──────────────────┐   inert or oxidizing        ┌──────────────────┐
│ PURE AND MIXED   │   atmosphere          ───▶  │ PURE AND MIXED   │
│ METAL CARBONATES │   ◀───                      │ METAL OXIDES     │
└──────────────────┘   carbon dioxide            └──────────────────┘
                       atmosphere
        
     carbon dioxide            oxidizing
     atmosphere                atmosphere

   reducing                          reducing
   atmosphere                        atmosphere

              ┌────────────────────────────┐
              │ METALS AND/OR METAL OXIDES │
              └────────────────────────────┘
```

The framework of interrelated heterogeneous solid state reactions and
their respective solid products.

The coprecipitation of aqueous solutions of metal salts with ammonium carbonate or alkaline metal carbonates represent the conventional route for the preparation of such mixed metal carbonates. Depending on the metal combinations as well as on the actual conditions, single phase solid solutions or bi- and multiphasic materials are obtained. The earth-alkaline metals Mg and Ca form solid solution carbonate precursors with a number of transition metals. Compounds such as $CaFe(CO_3)_2$ or $CaMn(CO_3)_2$ are typical representatives (ref. 7). Owing to the homogeneous atomic mixture in the parent structures, the diffusion distances during the thermal degradation leading to the formation of the respective ternary oxides are minimal. In the case of bi- or multiphasic carbonate precursors the diffusion distances are increased and the course of the product formation is therefore more complex.

The role of the ambient atmosphere as well as the actual pressure conditions during the decarbonatization influences the mechanistic course and thus the properties of the so-formed metal oxides decisively: It has been observed that depending on the partial pressure of CO_2 the temperature of the respective thermal decompositions varies within up to several hundred K (ref. 8). This phenomenon mainly originates from the reversibility of the decarbonatization process. In turn the reversibility gives rise to considerable sintering effects. This has been shown for the decomposition of calcite (ref. 9) as well as of other carbonates.

Only scarce knowledge exists on the *thermal reactivity of pure and mixed metal carbonates in reducing atmosphere*. As recent studies proved (ref. 10) earth-alkaline metal carbonates such as magnesite $MgCO_3$, dolomite $MgCa(CO_3)_2$ as well as calcite $CaCO_3$ decompose at comparably low temperatures when they get heated in reducing atmosphere, i.e. in molecular hydrogen. As simultaneous thermogravimetric / mass spectrometric measurements show, the main gaseous product is no more CO_2 but CO. Obviously, concomitant reduction processes take place. These phenomena, i.e. lowering of the decarbonatization temperature and partial reduction of the volatile carbonaceous compound get much more evident by thermally treating mixed earth-alkaline/transition metal carbonate precursors: Depending on the transition metal present in the parent material, remarkable decreases of the temperature onset are observed. More interestingly, different volatile products are obtained. By decomposing mixed Ca-Cu-carbonate precursors, the main volatile product is CO. From Ca-Co-carbonate precursors, mixtures of CO and CH_4 are formed and from Ca-Ni-carbonate, CH_4 is detected as main gaseous product. Finely dispersed elemental transition metals on CaO are obtained as solid products. Some of them prove to be active catalysts for the reduction of CO_2 with hydrogen under normal pressure (1 bar). In summary the well-controlled thermal degradation of pure or mixed metal carbonates allows the generation of a variety of interesting products such as pure or mixed binary and/or ternary metal oxides, as well as mixtures of metals and/or metal oxides. As it will be shown in the following, the reactive behavior of so-obtained metal oxides is equally differentiated.

In general, metal oxides prove to be stable up to comparatively high temperatures, when they are thermally treated in inert or oxidizing atmospheres. Their reactive behaviour changes drastically, however, if they are exposed to reducing atmospheres. As it has been shown for *perovskite-type metal oxides* with the general formula ABO_3 and adopting structures with predominantly isotropic character (ref. 11), the products of thermal reductions depend directly on the composition of the parent phases (ref. 12): Perovskites with transition metals such as Fe, Ni, Co, Mn or Cu in the B-position tend to form highly oxygen-deficient phases ABO_{3-x}. In many cases the course of the reduction is highly topotactic, i.e. the cation positions are conserved and the ordered oxygen vacancies lead to superstructures. Owing to the conservation of the fundamental structural features, these partly reduced oxides readily get reoxidized by forming the initial composition again. Such oxygen-deficient phases, however, can only be obtained, when the thermal treatment is performed under well-controlled experimental conditions, i.e. narrow temperature ranges and well-defined atmospheres. As an important feature, such reduction / reoxidation processes allow the modification of not only the atomic, but also of the electronic structures and thus of the physical properties. The catalytic potential of such phases, which reversibly release or take up oxygen, is a matter of detailed investigations (refs. 13, 14). In turn, at elevated temperatures or by reducing perovskitic metal oxides containing precious metals, mixtures of metals and metal oxides are generated. Again the temperature onsets of the respective reductions depend decisively on the composition of the parent materials.

In order to study influences of the compositional and structural features on the thermal reduction behaviour of mixed metal oxides, *delafossite-type phases* with the general formula $A(I)B(III)O_2$ have been studied in detail (ref. 15). They adopt a highly anisotropic layered structure (ref. 16-18), whereby linearly coordinated $A(I)$ metal cations are interlinking sheets of edge-sharing $B(III)O_6$ octahedra. The fact that a number of very different metal combinations can be stabilized in this structure, e.g. Cu^+, Ag^+ or Pd^+ occupying the A-positions and Fe^{3+}, Cr^{3+}, Al^{3+} or Rh^{3+} adopting the B-positions, renders these phases interesting with respect to physical and chemical properties. Moreover, it has been shown that isostructural quaternary phases with partly substituted A or B cations phases exist (ref. 19). In inert or oxidizing atmospheres, delafossites prove to be thermally stable. In molecular hydrogen, however, thermal degradation is observed. Again, the nature of the products as well as the reduction temperatures directly depend on metal combinations present in the parent phases. The metal selective thermal reduction behaviour of a variety of ternary and quaternary delafossites has been studied by quantitative thermogravimetry, temperature dependent X-ray diffraction and electron microscopy.

The thermal reduction of two delafossites containing B-cations with highly different properties, i.e. $CuAlO_2$ and $CuRhO_2$, as well as of respective quaternary phases $CuRh_xAl_{1-x}O_2$ has been studied (ref. 20). The temperature range of the respective reductions varies between ≈ 1000 K (for pure $CuAlO_2$) and ≈ 450 K (for pure $CuRhO_2$). Thermogravimetry reveals single step reductions of all quaternary phases. There is no indication for the formation of oxygen-deficient phases. As products, the following materials are generated:

- Starting with $CuRhO_2$, a metastable 1:1 CuRh alloy is formed, which segregates into a Cu-rich and a Rh-rich alloy upon heating to about 1000 K.
- Slow reduction (at lowest possible temperatures) of the quaternary phases leads to metallic Cu, CuRh alloy and X-ray amorphous alumina.
- From $CuAlO_2$, finely dispersed metallic Cu on alumina is obtained.

A similar reduction mechanism is observed for the isostructural series $CuRh_xCr_{1-x}O_2$ (ref. 21), which leads to a metastable CuRh alloy on corundum-type chromia.

In a series of further experiments, the influence of the type of A-cation on the reduction behaviour has been investigated: From $AgRhO_2$ ($T_{on} \approx 380$ K), a metastable AgRh alloy can be generated, which segregates into the elemental metals between 600 K and 650 K. The reduction of $PdRhO_2$ ($T_{on} \approx 420$ K) leads to the thermodynamically stable PdRh alloy.

The study of the thermal reducibility of delafossites with +II and +IV transition metal cations occupying the B-positions as e.g. $CuNi_{0.5}Ti_{0.5}O_2$ (ref. 21) gives evidence, how manifold the possibilities of different metal combinations really are. The course of the degradation ($T_{on} \approx 700$ K) is as follows:

$$CuNi_{0.5}Ti_{0.5}O_2 + H_2 \rightarrow 1.25\ Cu_{0.8}Ni_{0.2} + 0.25\ Ni + 0.5\ TiO_2 + H_2O$$
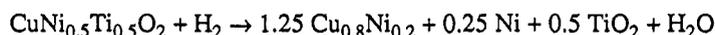
Compared with the respective binary metal oxides, this temperature accounts for a high stabilization of the present metal cations within the delafossite structure. Owing to the comparatively high reduction temperature, the products are formed as highly crystalline materials. As observed by scanning electron microscopy and – on a more informative level – by high resolution electron microscopy, the size and

the lattice perfection of the metal or alloy microcrystals formed during the abovementioned processes strongly depend on the reduction temperature. Under mild conditions, metallic particles with sizes well below 10 nm are readily obtained.

In summary, the mentioned reactions are of particular interest with respect to the preparation of finely dispersed metallic phases on alumina, chromia or titania. The knowledge of the experimental reduction parameters allows the control of the product formation. Thus, many of these delafossite phases represent integrated precursor systems for supported metallic or bimetallic catalysts (ref. 22). In fact, a so-formed Rh/Al$_2$O$_3$ product act as very efficient catalyst for the conversion of a CO$_2$/H$_2$ mixture into CH$_4$ at temperatures around 600 K. This feature leads back to the aforementioned catalytic properties of metal/metal oxide phases obtained from the reduction of mixed metal carbonates. It illustrates the potential applicability of heterogeneous solid state processes under well controlled experimental conditions.

INORGANIC COORDINATION COMPOUNDS AS PARENT MATERIALS OF METAL OXIDES AND METAL SULFIDES

Owing to their broad diversity of chemical composition as well as reactivity , inorganic coordination compounds represent widely applicable precursor phases for the thermal generation of binary or ternary transiton metal oxides, in some cases also metal carbides, and intimate mixtures of binary or ternary metal sulfides.

Starting thermal decomposition with e.g. compounds made up of complex copper(II) cations with amine ligands and chromate or dichromate anions such as Cu(pyridine)$_4$Cr$_2$O$_7$, Cu(NH$_3$)$_4$CrO$_4$, etc., i.e. 'mixtures of Cu and Cr on an atomic level', allows to vary systematically the Cu:Cr ratio in the resulting Cu-Cr-oxide products (ref. 5, 6, 23). The mechanistic course of the respective degradation processes finally leading to catalytically relevant phases as CuO, Cr$_2$O$_3$, CuCrO$_2$, CuCr$_2$O$_4$, and mixtures thereof, is usually complicated. In general, the first steps, i.e. the release of at least a part of amine ligands or the condensation of hydroxide groups, are stoichiometric, often topotactic, and easily interpretable by TG/MS investigations. Subsequently, however, superimposed or competing reactions are observed under evolution of O$_2$, N$_2$ and CrO$_3$. The so-formed intermediates are often amorphous and difficult to characterize. Continued heating leads to phase segregations, crystallizations and/or further degradations yielding the final products. The shape of the precursor crystals is roughly conserved during the various decomposition steps, i.e. more or less perfect pseudomorphs according to the parent crystals are obtained. The formation of cracks and pores, however, alters their microstructure considerably.

Recent studies on the thermochemical behaviour of a new copperdiammine vanadate, Cu(NH$_3$)$_2$(VO$_3$)$_2$, in various atmospheres (O$_2$, N$_2$,He, and H$_2$) (ref. 24) confirm the broad applicability of using amine complexes as precursors: Depending on the respective atmosphere, α- and β-CuV$_2$O$_6$ (oxidizing), Cu$_{0.95}$V$_2$O$_5$ (inert), and Cu° on V$_2$O$_3$ (reducing) are formed as product phases.

A scientific counterpart to the frequently observed situation -- formation of an interesting product by an ill-defined mechanism -- is contained in our previous work on nickel-thiocyanate-amine and nickel-platinum-cyanide-ammine complexes. These compounds were selected as model compounds, which allow a straightforward interpretation of the mainly topotactic decomposition mechanisms and the evaluation of specific kinetic data from thermogravimetric measurements (ref. 2). The products -- metal thiocyanates or metal cyanides -- of these well-understood reactions, however, are rather of purely scientific interest.

An important degree of freedom in using complex compounds as precursors is achieved by varying the size of the ligand molecules. This has been done systematically for the *preparation of vanadia* from novel ethylenediammonium- and propylenediammonium-vanadates (ref. 25 - 27). Catalytically active vanadia, V$_2$O$_5$, is conventionally prepared by thermal degradation of ammonium metavanadate, NH$_4$VO$_3$, which is built up of infinite chains of corner sharing VO$_4$-tetrahedra and ammonium cations. In principle, a vanadate adopting a chain structure can be transformed into the product V$_2$O$_5$ by a topotactic reaction mechanism, i.e. by structural conservation of the dominant chain elements. The condensation of these chains leads then to relatively crystalline vanadia with the well-known layered structure. In general, it can be expected that the smaller the cations separating the vanadate chains in the precursor are, the better is the chance for a topotactic course of the reaction and thus, the higher is the crystallinity of the product. If, therefore, a *most active vanadia* is strived for, relatively spacious cations should separate the vanadate chains in the precursor. Moreover, these cations should be completely

evolved at comparatively low temperatures. These considerations led us to the preparation of two novel precursors for vanadia:

- ethylenediammonium-vanadate, $(NH_3\text{-}CH_2\text{-}CH_2\text{-}NH_3)^{2+}(VO_3)_2{}^{2-}$, and
- propylenediammonium-vanadate, $(NH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_3)_2{}^{2+}(V_2O_7)^{4-}\cdot3H_2O$.

The structure of ethylenediammonium-vanadate is made up of the expected infinite VO_3-chains running parallel to the c-axis, and of doubly protonated ethylenediamine (= en) units located between them. The thermal behaviour was investigated from ambient temperature up to $\approx$ 870 K by thermogravimetric/mass spectrometric measurements. As the product formation directly depends on the ambient atmosphere, comparative experiments were carried out in nitrogen and oxygen.

In flowing oxygen en-vanadate decomposes in two steps in the temperature range of $\approx$ 470 K and $\approx$ 720 K. The detailed analysis of the mass spectrometric measurements reveals that the organic cation is completely degraded within the solid during the heat treatment. Temperature dependent X-ray diffraction further confirmed the intermediate formation of V_3O_7 and V_4O_9. Thus, the organic cation gets at least partially oxidized by oxygen of the vanadate units.

As a surprising fact, large amounts of water are formed during the decomposition of the mentioned precursor in pure nitrogen. Again, one has to conclude that oxygen of the vanadate units takes part in the reaction. According to temperature dependent X-ray diffraction, the system gets amorphous at $\approx$ 450 K. As final oxidic product, V_2O_4 is obtained in the temperature range of 920 K. Cooling down the sample to 770 K and reheating it in pure oxygen results in the evolution of CO_2 and in an increase of the weight up to stoichiometric V_2O_5. Thus, an X-ray amorphous carbide is generated by the described degradation in a nitrogen atmosphere. The degradation of en-molybdates yielded analogous results (ref. 28).

The crystal structure of the propylenediammonium vanadate precursor is made up of individual $V_2O_7{}^{4-}$ ions forming layers parallel to the a-c-plane with the water molecules (ref. 27). These layers are separated by the propylenediammonium cations. Owing to these structural features, the propylendiammonium precursor exhibits a thermal behaviour, which is distinctly different of the one found for en-vanadate: Decomposition starts well below 370 K and propylenediamine as well as water are registered as volatile products. After a sudden release of CO_2 at $\approx$ 720 K, V_2O_5 is obtained. As a consequence of the particularly large organic cations separating the vanadate units in the precursor, the pseudomorphous product is built up of non orientated, comparably small vanadia crystallites with dimensions in the order of $\approx$ 100 nm. The size of the vanadia crystallites obtained from the en-vanadate precursor is increased by about one order of magnitude, but still considerably smaller than the one obtained from the conventional metavanadate precursor.

Investigations on the formation of similarly microcrystalline molybdena, MoO_3, support the described considerations: An ethylenediammonium molybdate has been prepared, which contains isolated monomolybdate units. The conventional precursor for molybdena is a condensed heptamolybdate.

The thermal decomposition of complexes with the general formula $M(L)_nM'S_4$ (M = transition metals such as Mn, Co, Ni, Cu, Zn; L = $NH_4{}^+$, NH_3, ethylenediamine (en), diethylenetriamine (dien); M' = Mo, W) can be used for the generation of *ternary metal sulfides* or *intimately mixed domains of binary metal sulfides*. Considering the importance of the most active hydrodesulfurization catalysts, i.e. MoS_2 and WS_2 promoted with various transition metal sulfides of e.g. Co or Ni, the decomposition of the abovementioned complexes are well-suited for the controlled generation of such materials. In contrast, the conventional methods of preparation allow only limited insights into the processes of formation of the catalytically active species. Therefore, the systematic variation of the precursor composition, i.e. of the metal combinations as well as the ligands, was used for controlled alterations of the degradation mechanism and thus for directly influencing the properties of the so-formed products (ref. 29). In addition, this approach allowed a detailed characterization of the role of the experimental conditions, in particular of the gas atmosphere.

Starting with copper ammonium thiometallates, $CuNH_4M'S_4$, as precursor phase (ref. 30), microcrystalline ternary metal sulfides are obtained by a topotactic decomposition in inert gas atmosphere. By decomposing ammine precursors such as $M(NH_3)_6M'S_4$, amorphous ternary intermediates are observed. The most interesting and rather specific property of these microcrystalline or amorphous ternary sulfide phases is revealed by differential thermal analysis: A pronounced exothermal signal is registered in a temperature range, where no weight loss occurs. This phenomenon is explained by phase segregation processes leading to the respective binary sulfides MS, and intermediately, to $M'S_3$. Under subsequent loss of elemental sulfur, intimately intergrown mixtures of the thermodynamically stable sulfides MS_{1-x} and $M'S_2$ are obtained as final decomposition products. The mass spectrometric detection of evolved products as well as powder X-ray diffractometry confirm these

findings. The degradation of the complexes containing en or dien as ligands starts at comparatively lower temperatures. There is no evidence for the existence of intermediate ternary sulfides as no exothermal DTA signals are found. As final products, however, similarly textured materials are formed.

In order to get detailed information on the microstructure of these product phases, scanning and high resolution electron microscopic studies were carried out: In general, the contours of the precursor crystals get preserved all over the degradation, i.e. the final products are forming characteristic pseudomorphs.Their microstructure is made up of intergrown crystalline domains with dimensions in the range of $\leq$ 10 nm. In the Cu-Mo-S-system, as a consequence of the topotactic structural reaction mechanism to the mentioned crystalline intermediate, the product domains of the binary sulfides adopt a relative mutual orientation.

The influence of the selected ligands on the product formation, i.e. of NH_3, en and dien in the parent phases, is reflected by the different microstructures of the final products: Owing to the amorphous character of the intermediate ternary sulfide obtained from the precursors containing NH_3, the intergrown domains of the final products adopt no mutual orientation and they are smaller as the ones of the Cu-Mo-S-system. Starting with en or dien complexes, decomposing without formation of any ternary sulfide phases is registered. The intergrown fragments of the resulting binary sulfides are still smaller ($\leq$ 5 nm) and they adopt highly disordered structural features.

CONCLUSIONS

The described studies lead to the following statements: Conventional thermal analysis represents a widely applicable tool for the measurement of quantitative compositional changes as well as of thermal properties of solids. Monitoring heterogeneous solid state reactions in dependence of the ambient gas atmosphere and/or gas pressure yields more specific informations on the thermal reactivity of condensed matter. However, detailed insights into the mechanistic course on a microscopic, i.e. atomic scale require not only the knowledge of structural changes and/or relationships between parent, intermediate and final products, but also the qualitative analysis of the volatile products. Consequently, temperature dependent X-ray diffraction and simultaneous mass spectrometry or gas chromatography are indispensable complementary methods of investigation.

Based on the data obtained from the mentioned means, the *'real structure'* of the final products comprising their compositional, structural and morphological properties has to be correlated with the ones of the parent materials as well as with the degradation mechanism leading to their formation. Therefore, results obtained from optical microscopy, scanning and high resolution electron microscopy are important complements for describing heterogeneous solid state reactions as well as for understanding the interdependence of microscopic and macroscopic mechanistic processes. High resolution electron microscopic imaging and selected area diffraction are particularly well-suited techniques for the characterization of extremely small particles or of microdomains in multiphasic solid products.

Together with energetic criteria, the mentioned concept represents a promising basis for the controlled modification of specific properties of product phases, e.g. of thermodynamically metastable compounds such as the described bimetallic phases on oxidic supports from the thermal reduction of delafossite-type metal oxides, or ternary metal sufides from the thermal degradation in inert atmosphere of complex transition metal amine thiometallates. In turn, such alternate synthetic pathways lead to mono- or multiphasic materials, which may be thermodynamically stable, but inaccessible by conventional preparative techniques.

In summary, the best possible comprehension of the thermochemical reactivity of solids is the prerequisie for the preparation of products exhibiting optimized properties with respect to their applicability in e.g. heterogeneous catalysis or materials science.

REFERENCES

1. Scientific American: special issue on 'Materials for Economic Growth', Scient. Amer., 255, 42 - 177 (1986).
2. A. Reller and H.R. Oswald, J. Solid State Chem., 62, 306 - 316 (1986).
3. H.R. Oswald and A. Reller, J. Thermal Anal., in press (1988).
4. H.R. Oswald and J.R. Günter, Mat. Sci. Monogr., 28A, 101 - 108 (1985).

5. H.R. Oswald and A. Reller, Ber. Bunsenges. Phys. Chem., 90, 671 - 676 (1986).

6. H.R. Oswald and A. Reller, Thermochim. Acta, 95, 311 - 318 (1985).

7. K. Vidyasagar, J. Gopalakrishnan and C.N.R. Rao, Inorg. Chem., 23, 1206 - 1210 (1984).

8. M. Maciejewski and A. Reller, Thermochim. Acta, 110, 145 - 152 (1987).

9. M. Maciejewski and H.R. Oswald, Thermochim. Acta, 85, 39 - 42 (1985).

10. A. Reller, C. Padeste and P. Hug, Nature, Lond., 329, 527 - 528 (1987).

11. J.B. Goodenough and J.M. Longo,A.F. Wells, Landolt-Börnstein, Group III, Vol. 4a, Springer-Verlag, Berlin (1970).

12. A. Reller, Ber. Bunsenges. Phys. Chem., 90, 742 - 745 (1986).

13. R.J.H. Voorhoeve, Advanced Materials in Catalysis, eds. J.J. Burton and R.L. Garten, Academic Press, New York (1976).

14. A. Reller, J.M. Thomas, D.A. Jefferson and M.K. Uppal, Proc. R. Soc. Lond., A394, 223 - 241 (1984).

15. P. Kuhn, Ph.D. Thesis, University of Zürich, (1988).

16. R.D. Shannon, D.B. Rogers and C.T. Prewitt, Inorg. Chem., 10, 713 - 718 (1971).

17. C.T. Prewitt, R.D. Shannon and D.B. Rogers, Inorg. Chem., 10, 719 - 723 (1971).

18. D.B. Rogers, R.D. Shannon, C.T. Prewitt and J.L. Gillson, Inorg. Chem., 10, 723 - 727 (1971).

19. J.-P. Doumerc et al., J. Phys. Chem. Solids, 48 37 - 43 (1987).

20. P. Kuhn, A. Reller and H.R. Oswald, J. Less-Common Met., 137, 231 - 239 (1988).

21. H.R. Oswald, P. Kuhn and A. Reller, Solid State Ionics, in press (1988).

22. J.H. Sinfelt, Bimetallic Catalysts, Wiley & Sons, New York (1983).

23. N. Seferiadis, Ph.D. Thesis, University of Zürich (1987).

24. S. Aschwanden, Ph.D. Thesis, University of Zürich, in progress.

25. P. Hug, Ph.D. Thesis, University of Zürich, in progress.

26. W. Bensch, P. Hug, A. Reller and H.R. Oswald, Mater. Res. Bull., 22, 577 - 583 (1987).

27. W. Bensch, P. Hug, A. Reller and H.R. Oswald, in preparation.

28. W. Bensch, P. Hug, R. Emmenegger, A. Reller and H.R. Oswald, Mater. Res. Bull., 22, 447 - 454 (1987).

29. H.R. Oswald, G. Stauber-Reichmuth and A. Reller, Solid State Ionics, in press (1988).

30. W. Bensch, G. Stauber-Reichmuth, A. Reller and H.R. Oswald, Rev. Chim. Min., 24, 503 -508 (1987).