Thermochimica Acta, 95 (1985) 311—318
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMAL ANALYSIS AS A TOOL FOR INVESTIGATIONS IN METAL OXIDE CHEMISTRY *

H.R. Oswald and A. Reller
Institute for Inorganic Chemistry, University,
Winterthurerstrasse 190, CH-8057 Zürich (Switzerland)

ABSTRACT

Applications of thermoanalytical methods for the controlled preparation of metal oxides from various initial compounds ('precursors') as well as for investigations of physical properties and the chemical behaviour of oxidic phases as function of temperature and atmosphere are presented. Studies elucidating the course of such processes yield important contributions to the understanding of the reactivity of solids in general. Moreover, they are, e.g. in the field of heterogeneous catalysis, of practical relevance. It is shown, however, that the capability of mere thermal analysis suffers from limitations which have to be overcome by using additional, independent methods such as X-ray diffraction as well as light and electron microscopy.

INTRODUCTION

An essential part of inorganic solid state chemistry is concerned with metal oxides. Investigations into oxidic phases have been and unvariably still are of central importance for the understanding of the reactivity of solids in general. I may, in this context, respectfully point at the abundance of valuable contributions to the preparative and structural chemistry of metal oxides as well as to the establishment of solid state chemistry which originates from representatives of Swedish research schools.

Beyond their significance in fundamental research, further motives to deal with oxides get evident from applied chemistry, as oxidic phases are e.g. important as corrosion products, electronic and magnetic materials, pigments and, last but not least, catalysts.

---

* As parts of the work used for this lecture have been or will be published elsewhere or still are in progress, this succinct version aims in emphasizing the principal views of the authors rather.

0040-6031/85/$03.30

For the preparation of oxides it must be taken into account that a given phase is by far not completely described by its chemical composition and crystal structure only. The pronounced inherent non-isotropy of the chemical (as well as physical) properties of most solids, which can in particular cause promotion resp. inhibition of processes occurring at certain crystallographic sites requires by force additional morphological information rather.

Keeping in mind such correlations, it is particularly interesting to study the generation of metal oxides by carefully controlled thermal decomposition of suitable initial materials, so called 'precursors' (refs. 1, 2), a classical topic which has gained new attention under the modern term 'soft chemistry'. Thus, heterogeneous solid state reactions, in the simplest case of the type:

$$A_{solid} \rightarrow B_{solid} + C_{gaseous}$$

have to be investigated. Typical solid initial compounds may be:

- hydroxides, hydroxide salts of metals;
- metal salts and their hydrates;
- metal complexes with e.g. amine ligands.

Evidently, thermoanalytical methods as TG, EGA, DSC/DTA can yield substantial contributions to such studies. As, however, these reactions mostly consist of several interdependent, simultaneously and/or consecutively occurring processes, a sum of experimental data is required for a consistent interpretation. By means of independent and complementary techniques the following qualitative and quantitative informations have to be achieved:

- The structural reaction mechanism is determined from investigations of structural changes occurring during the course of the heterogeneous solid state reaction.
- Correlations of structural and morphological information give evidence for the macroscopic reaction mechanism, which describes the over-all reaction of one particle or of a sum of particles as function of the experimental conditions.
- Time- and temperature-dependent quantitative thermoanalytical measurements combined with simultaneous analysis of volatile products yield the necessary data for the determination of compositional and energetic changes.

The evaluation and interpretation of the kinetics finally have to be based on the correlation of the above mentioned quantitative thermoanalytical results with the qualitative informations from appropriate techniques such as X-ray measurements, light and electron microscopy a.s.o.

In the further parts of this lecture, the expressed ideas are first illustrated by examples where the oxide phase(s) appear on the product side. Subsequently, the role of thermal analysis as a tool to investigate some physical and chemical properties of mixed metal oxides as initial phases will be shown.

PREPARATION OF METAL OXIDES FROM PRECURSOR PHASES

The preparation of molybdenum trioxide from its hydrates is well suited to illustrate how simple thermogravimetric curves contribute to the description of solid state reactions. Single crystals of $MoO_3 \cdot 2H_2O$ decompose in two well separated steps first to yellow $MoO_3 \cdot H_2O$ and then to MoO_3. As scanning electron microscopy and X-ray techniques reveal, the intermediate and final phases exhibit quite perfect pseudomorphs with a high degree of crystallographic orientation, resulting in an oxide built up of stacked lamellae (010). This is a typical example of topotaxy (refs. 3, 4, 5), and the structural study of the initial and final phases in their relative orientation did not only allow to recognize the role of corner linked octahedra as the dominating element in the structural reaction mechanism, but also to propose a plausible structure for the intermediate (ref. 6).

If $MoO_3 \cdot H_2O$ is grown from solution, a white, needle shaped polymorph is obtained which decomposes on the thermobalance to pseudomorphs built up of MoO_3 crystallites in a distinctly different crystallographic orientation. The detailed study of the structural reaction mechanism, in this case governed by double chains of edge-linked octahedra extending parallel to the needle axis, allowed a correct prediction of the structure of white $MoO_3 \cdot H_2O$ (ref. 7).

Detailed mechanistic and kinetic studies on thermal decompositions of selected single crystalline metal complexes exhibiting a high degree of topotaxy gave evidence that in cases, where the gaseous products are evolved into spaces between orientated lamellae or fibres, phase boundary reactions, i.e. bond breakages, and not diffusion controlled processes are the rate limiting steps (ref.8).

For the formation of oxides by thermal decomposition of metal hydroxides, several examples have been studied with respect to structural and morphological features. It turned out that the highest degree of topotaxy for sequences such as $Cu(OH)_2 \rightarrow CuO \rightarrow Cu_2O$, or

γ- resp. β-$Zn(OH)_2$ → ZnO is attained if the respective decompositions are performed under high vacuum, e.g. by in situ electron microscopical experiments (see e.g. ref. 9).

Our recent interests focus onto the preparation of mixed metal oxides (resp. chalcogenides) of catalytical relevance. By decomposing precursor phases containing the metals as 'atomic mixture', the observed extent of the decrease in the temperatures of formation of certain oxidic phases is remarkable indeed (see e.g. $Sr_2[Cu(OH)_6] \rightarrow Sr_2CuO_3 + 3H_2O$ at 400°C, compared to 1100°C for the synthesis from SrO and CuO, ref. 10).

The detailed elucidation of the occurring processes is, however, by far not trivial. Insights into the complex nature of the respective phenomenology result from current work in the field of copper-chromium oxides. As precursor compounds, a number of compositionally and structurally well defined crystalline complexes with several Cu(II) to Cr(VI) ratios and different ligands are investigated with respect to their thermal decomposition (ref. 11). For the explanation of compositional changes proceeding with first steps of degradation, i.e. the release of ligands such as H_2O, NH_3 or pyridine, thermogravimetry combined with mass spectrometry proves to be a most suitable tool. Very often, however, there arise considerable problems to interpret the course of subsequent, simultaneously and/or consecutively occurring processes, where e.g. H_2O, O_2, N_2 (from NH_3!) and CrO_3 are evolved and poorly defined intermediates or mixtures of several, even non-stoichiometric oxide phases are formed. Obviously, mere thermoanalytical measurements do not allow the deduction of unambiguous reaction mechanistic results. Therefore, additional informations have to be acquired by e.g. temperature dependent X-ray diffraction, electron microscopy, spectroscopy as well as accurate chemical analyses. In this context, it has been observed in many cases, that due to the release of ligands X-ray amorphous, but nevertheless highly pseudomorphous intermediates are formed. At more elevated temperatures, crystallization, phase segregation and/or further degradation processes take place, during which the shape of the initial crystals, although exhibiting cracks or pores, remains conserved. The question arises whether the concept of topotaxy still allows appropriate explanations for such processes. Nevertheless, an even distribution of metal cations in the X-ray amorphous intermediates can be considered as result of the actual course of the respective degradations. Indeed, mixed Cu-Cr-oxides such as $CuCr_2O_4$ or intimate mixtures of $CuCr_2O_4$ and CuO are active catalysts for the selective hydrogenation of carbonyl compounds, as well as for the oxidation of carbon monoxide.

CONTRIBUTIONS OF THERMAL ANALYSIS TO INVESTIGATIONS ON THE REACTIVITY OF METAL OXIDES

Apart from the problems of controlled syntheses of metal oxides with characteristic compositions, structures and morphologies, their respective reactivities as function of temperature and/or ambient atmosphere are of crucial interest. Possible processes occurring may be described by the following general equation:

$$\Sigma A_{solid} + \Sigma B_{gaseous} \rightleftarrows \Sigma C_{solid} + \Sigma D_{gaseous}$$

In the simplest case, solid-solid phase transitions can be investigated as function of temperature and composition: As example, how compositional features influence the temperature dependence of such a process, the phase transitions of Mn_3O_4 (hausmannite) and the solid solutions $Mn_xCr_{3-x}O_4$ have been studied by means of thermogravimetry and differential thermal analysis. It is well known, that Mn(III) compounds undergo so called Jahn-Teller phase transitions', during which a low temperature phase with ordered, statically distorted coordination octahedra passes into a dynamically symmetrized high temperature form. For the pure manganese spinel Mn_3O_4 this dynamization, which is concomitant with a phase transition from a tetragonal to a cubic structure, occurs at 1178°C with an enthalpy change of 82 J/g. The substitution of Mn(III) by increasing amounts of Jahn-Teller inactive Cr(III) leads to a steady decrease of the temperature of the reversible phase transition (ref. 12). Moreover, it has been detected by simultaneous TG/DTA measurements, that during the respective phase transitions considerable weight losses are registered. This phenomenon is explainable by a sudden release of mechanical tensions within the crystallites, which effectuates, that small fragments literally jump out of the crucible (ref. 13).

Whereas these investigations rather emphasize the interdependence of composition and thermal behaviour of metal oxides, the following examples shall demonstrate the role of the ambient atmosphere in the field of the chemical reactivity of this class of compounds.

If metal oxides are heated in vacuum, oxygen, air or any inert gas atmospheres, they usually prove to be stable, unless melting, sublimation or decomposition processes and phase segregations take place. In reducing atmospheres, however, oxygen is released and, depending on the actual compositions, non-stoichiometric, oxygen deficient phases or elemental metals are formed.

For $CaMnO_3$ and Ca_2MnO_4, two members of a large group of ternary oxides crystallizing in the structure of the naturally occurring mineral perovskite $CaTiO_3$ respectively the related K_2NiF_4 structure, it has been observed by quantitative thermogravimetric experiments performed under hydrogen, ammonia or C_2H_4, that reduction processes take place at relatively low temperatures whereby grossly oxygen deficient phases are formed (ref. 14). By means of spectroscopical techniques, X-ray diffraction and high resolution electron microscopy it has been established, that several distinct phases with stoichiometries between $CaMnO_3$ and $CaMnO_{2.5}$ respectively Ca_2MnO_4 and $Ca_2MnO_{3.5}$ are formed. The structures of these intermediates are made up of corner-linked $Mn(IV)O_6$ octahedra and $Mn(III)O_5$ square pyramids. The structural frameworks of the initial phases, i.e. the cation positions, are preserved. Topotactical features account well for the ease of the reoxidation, which leads to the formation of the initial, fully oxidized compounds. Such kind of metal oxides, which permit reversible loss and uptake of oxygen are important due to their potential relevance as materials with highly selective catalytical activities (ref. 15).

By heating $CaMnO_{2.5}$ respectively $Ca_2MnO_{3.5}$ in reducing atmospheres up to 550°C CaO / MnO respectively 2CaO / MnO are formed as biphasic materials. The fact that these mixed phases undergo reoxidation to the initial products at relatively low temperatures cannot be explained by the preservation of the structural framework. As it has been verified by electron microscopy, this phenomenon has to be assigned to the existence of very small, intimately mixed crystallites. Within these crystallites the metal cation positions differ from their positions in the phases $CaMnO_3$ respectively $CaMnO_{2.5}$ and Ca_2MnO_4 respectively $Ca_2MnO_{3.5}$, but the diffusion paths, which the cations have to undergo during the reoxidation are very short (ref. 16).

$CaRuO_3$, a perovskite related mixed oxide with a precious metal in the B cation position exhibits a similar reduction/reoxidation behaviour as the aforementioned calcium-manganese-oxides. As it has been determined by quantitative thermogravimetric measurements and X-ray diffraction, however, the full reduction of this compound leads to the formation of calcium oxide and finely dispersed ruthenium metal particles. This biphasic product, in turn, undergoes reoxidation at low temperatures, and the initial perovskite is formed again. By repeating the reduction/reoxidation processes, the size of the Ru° crystallites can be decreased to diameters below 50 Å, and they only are detectable by high resolution electron microscopy (ref. 17).

In comparison to the above mentioned perovskite related compounds with rather isotropic structures and physical properties, the highly anisotropic delafossite related ternary metal oxides $A(I)B(III)O_2$, e.g. $CuAlO_2$ and $CuRhO_2$, show a distinctly different reactivity: Thermogravimetry under reducing atmosphere proves, that $CuAlO_2$ as well as $CuRhO_2$ only get reduced above 600°C, single crystals only above 700°C. The reduction leads to the formation of metallic copper and alumina respectively rhodia. In contrast to the fully reduced biphasic products obtained from the reduction of perovskite related initial products, these mixtures get reoxidized without forming the initial delafossite phases, i.e. the A metal cation only undergoes reoxidation (ref. 18).

CONCLUDING REMARKS

As it has been shown by examples of preparation from precursor systems as well as chemical reactions of metal oxides, thermoanalytical measurements performed under controlled experimental conditions allow accurate determinations of e.g. compositional changes of stoichiometrically well defined reactions. Quite often, however, simultaneous and interdependent processes take place, for which the thermoanalytically obtained over-all measurements cannot yield unambiguous interpretations. Obviously, additional informations have to be acquired by different independent methods of investigation (see also ref. 19).

These statements are of particular importance in the field of the solid state chemistry of metal oxides, inasmuch as very often non-stoichiometric phases and/or multiphasic products are observed.

A best possible understanding of the actual mechanistic features characterizing respective processes is an indispensable prerequisite for any determination of meaningful kinetic parameters from thermal analysis (ref. 20).

ACKNOWLEDGEMENT

Financial support from the "Swiss National Science Foundation" under project nr. 2.023-0.83 is gratefully acknowledged.

REFERENCES

1 J.M. Longo, H.S. Horowitz and L.R. Clavenna, in S.L. Holt, J.B. Milstein, M. Robbins (Eds.), Solid State Chemistry: A Contemporary Overview, Adv. in Chem. Ser. 186, Am. Chem. Soc., Washington, D.C., 1980, pp. 139-150.
2 A. Wold, J. Chem. Ed., 57 (1980) 531-536.
3 J.R. Günter and H.R. Oswald, Bull. Inst. Chem. Res. Kyoto Univ., 53 (1975) 249-255.
4 H.R. Oswald and J.R. Günter, in E. Kaldis and H.J. Scheel (Eds.), 1976 Crystal Growth and Materials, North-Holland, Amsterdam, 1977, pp. 416-433.
5 H.R. Oswald and J.R. Günter, Reactivity of Solids, Proceedings of the 10th Int. Sympos. on the React. of Solids, Univ. of Dijon, 1984, Elsevier, Amsterdam, in press.
6 J.R. Günter, J. Solid State Chem., 5 (1972) 354-359.
7 H.R. Oswald, J.R. Günter and E.Dubler, J. Solid State Chem., 13 (1975) 330-338.
8 H.R. Oswald, A. Reller and M. Maciejewski, Thermochim. Acta, 72 (1984) 139-146; A. Reller and H.R. Oswald, J. Therm. Anal., 29 (1984) 1013-1016; id., submitted to J. Solid State Chem.
9 H.R. Oswald and R. Asper, in R.M.A. Lieth (Ed.), Preparation and Crystal Growth of Materials with Layered Structures, Reidel, Dordrecht, 1977, pp. 71-140.
10 P. Korber, Ph.D. Thesis, Univ. of Zürich, 1974.
11 N. Seferiadis, Ph.D. Thesis, Univ. of Zürich, in progress.
12 P. Holba, M. Nevřiva and E. Pollert, Mat. Res. Bull., 10 (1975) 853-860; H.R. Oswald, J.P. Matthieu and M. Wirz, Thermochim. Acta, 20 (1977) 23-25.
13 A. Lüscher, Ph.D. Thesis, Univ. of Zürich, 1983.
14 K.R. Poeppelmeier, M.E. Leonowicz and J.M. Longo, J. Solid State Chem., 44 (1982) 89-98.
15 A. Reller, J.M. Thomas, D.A. Jefferson and M.K. Uppal, Proc. Roy. Soc. Lond., A 394 (1984) 223-241.
16 A. Reller, G. Davoodabady and H.R. Oswald, Thermochim. Acta, 83 (1985) 121-124.
17 A. Reller, Reactivity of Solids, Proceedings of the 10th Int. Sympos. on the React. of Solids, Univ. of Dijon, 1984, Elsevier, Amsterdam, in press.
18 P. Kuhn, Ph.D. Thesis, Univ. of Zürich, in progress.
19 W.E. Brown, D. Dollimore and A.K. Galwey, in C.H. Bamford and C.F.H. Tipper (Eds.), Chemical Kinetics, Vol. 22: Reactions in the Solid State, Elsevier, Amsterdam, 1980, pp. 283-287.
20 H.R. Oswald and A. Reller, in Mat. Sci. Monogr. 10, K. Dyrek, J. Haber and J. Nowotny (Eds.), Elsevier, Amsterdam, PWN Warszawa, 1982, pp. 964-967.