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STRUCTURE AND FORM OF SOLIDS AS RULING FACTORS FOR THEIR THERMOCHEMICAL REACTIVITY

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The role of structural parameters strongly influencing the course of heterogeneous solid-state reactions is established. Owing to the close relationship between the form and reactivity of solids, due emphasis must be given to detailed morphological studies. This allows the derivation of consistent correlations between the reaction mechanism on a microscopic scale and the observed macroscopic changes.

Our present interests are focused on the generation of solids with "tailor-made" specific chemical and physical properties. Starting with suitable precursors and appropriately selected experimental conditions, in particular with reactive gases such as molecular hydrogen, the controlled preparation of, for example, catalytically active finely dispersed metals or alloys, and also binary and ternary metal oxide and sulfide phases is demonstrated.

As indispensable tools, thermoanalytical techniques are applied in combination with mass spectrometry and gas chromatography.

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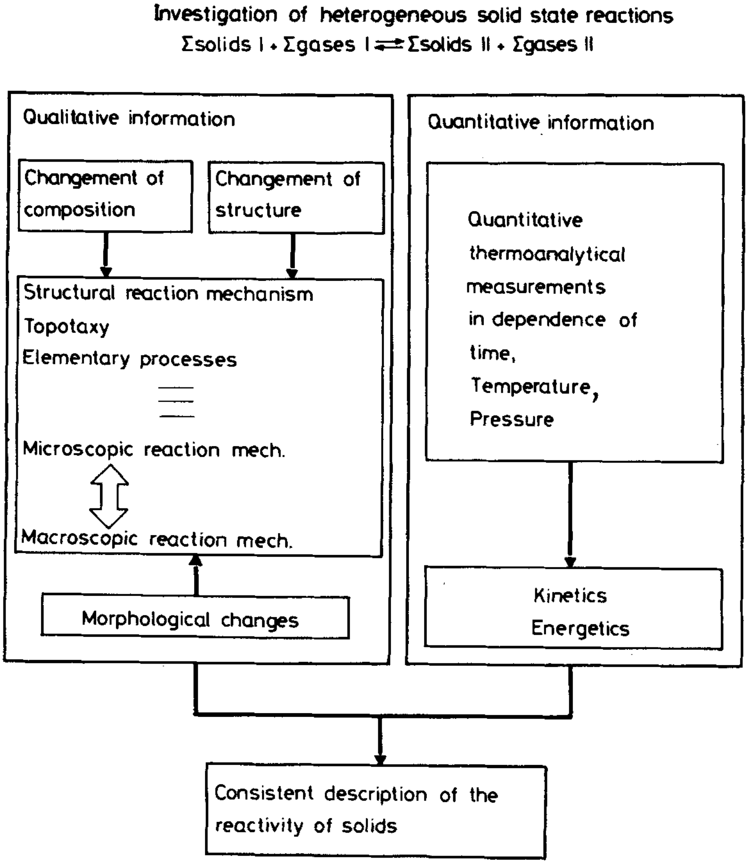
The characterization of the thermal reactivity of solid materials represents a topic of general importance ranging from fundamental scientific aspects to application-orientated problems. Whereas in the field of pure science, the interests are focussed on the mechanistic course, the kinetics or the thermodynamics of solid state reactions, the generation of 'tailor made' materials with specific chemical and/or physical properties at optimum conditions is of crucial relevance for technical and industrial thermochemical processes. In both cases, however, the complex nature of the solid with all its various features, i.e. its actual form, has to be taken into consideration. As a matter of fact, a solid is by far not entirely characterized by defining its chemical composition and its crystal structure. Solids react as 'individuals', and thus their reactive behavior in relation to 'partners' turns out to be accordingly manifold, differentiated, often hard to understand, and therefore challenging. Examples of properties constituting the individuality of solids comprise:

- size and shape of particles
- crystallographic faces making up the surface,
- domain structure, texture, etc.

Therefore, a consistent description of solid matter affords complementary methods of investigation. Moreover, the study of solid state processes, i.e. phase transitions, thermal decompositions of solids or reactions of solids with gases, comprises a detailed characterization of initial materials, possible intermediates as well as of the solid and volatile products being involved. In fact, the mere registration of compositional changes e.g. by thermogravimetry allows only limited insights into a given process. Apart from performing quantitative thermoanalytical measurements on defined samples and under carefully controlled conditions, concomitant structural and morphological studies have to be carried out. Only this kind of approach (Scheme 1) allows consistent correlations between the reaction mechanism on a microscopic scale with the observed macroscopic changes.

In previous studies, the role of structural and morphological parameters strongly influencing mechanism and kinetics of heterogeneous solid state reactions has been emphasized [1,2]. Based on this knowledge, the aim of our present work is focussed on the controlled preparation of solids such as metal oxides, binary and ternary sulfides as well as finely dispersed metals and alloys. As a matter of fact, such products are often metastable or tend to undergo sintering of phase segregations at elevated temperatures. Thus, the use of suitable precursor systems in order to produce interesting inter-



mediate or product compounds as a result of thermal degradation at relatively low temperatures represents an appropriate choice. Depending on the desired form of the final products, the selection of the initial materials is of decisive significance.

In the following, these statements get illustrated by representative examples, emphasizing the impacts of compositional, structural and morphological features as ruling factors for the reactivity of solids.

Results and discussion

Preparation of vanadia from novel ethylenediammonium- respectively propylenediammonium-vanadates.

Vanadia is conventionally prepared by thermal degradation of ammonium metavanadate NH_4VO_3 [3]. In order to study the influence of different ammonium cations on the formation of the solid product, comparative investigations on the thermal behavior of two novel precursors, i.e. ethylenediammonium-vanadate $(NH_3{-}CH_2{-}CH_2{-}NH_3)^{2+}((VO_3)_2)^{2-}$ [4] respectively propylenediammonium-vanadate $((NH_3{-}CH_2{-}CH_2{-}CH_2{-}NH_3)_2)^{4+}(V_2O_7)^{4-}.3H_2O$ [5] have been performed. The reason to choose such comparably spacious cations was to enhance the distances between the vanadate units in the initial phases and thus to alter the course of the respective decompositions. Due attention has been paid to the role of the atmosphere by thermogravimetric/mass spectrometric (TG/MS) measurements in nitrogen and in oxygen [6]. Independent of the atmosphere, TG/MS results for ethylenediammonium-vanadate reveal a multistep degradation, during the course of which, however, no ehylenediamine is detected, but only primary or secondary fragments such as H_2O, CO_2, NO and NH_3. The fact, that in nitrogen atmosphere large amounts of water are evolved, gives rise for the assumption, that oxygen of the vanadate groups takes part in the reaction. This has been proven by powder X-ray analysis of the final products, revealing the presence of partly reduced oxide phases such as V_2O_4. In addition, this oxide is transformed into pure vanadia by controlled heat treatment on the thermobalance under oxidizing atmosphere. For propylenediammonium-vanadate a multistep decomposition is observed too. But in contrast to ethylenediammonium-vanadate, the reaction starts at lower temperature ($< 100^\circ$) and produces some undecomposed propylenediamine, accompanied by water, during the first step. The final product is also vanadia. Depending on the initial materials the morphology of the final products varies to a remarkable extent: Pseudomorphs made up of vanadia crystallites with dimensions below 1 μm are obtained from thermally decomposed ethylenediammonium-vanadate crystals. As a consequence of the presence of particularly large cations besides structurally isolated, only dimeric vanadate groups in the crystal lattice of the propylenediammonium-vanadate, the so produced vanadia is made up of agglomerated microcrystals which are nearly one order of magnitude smaller than those from the ethylenediammonium salt.

It has been shown recently that ethylenediammonium salts are suitable precursors for the generation of microcrystalline molybdenum (VI) oxide as well [7].

Preparation of ternary sulfides of molybdenum and tungsten as metastable intermediates, and of finely dispersed mixtures of the respective binary sulfides.

Mixtures of MoS_2 or WS_2 with sulfides of various transition metals e.g. Co and Ni, are efficient hydrodesulfurization catalysts [8]. In general, they are generated in situ or by impregnation of appropriate support materials. These methods, however, allow only limited insights into the process of formation and thus few possibilities of controlling important product properties such as exact composition or domain structures. Therefore, we have chosen solid state decomposition reactions of selected complex compounds, which enable a systematic variation of compositional features, i.e. metal combinations and ligands. In addition, this approach allows a detailed characterization of the role of experimental conditions.

As initial materials, solid complexes of the general formula $ML_nM'S_4$ were prepared, where M = Mn, Co, Ni, Zn; L = NH_3, en (ethylenediamine) and M' = Mo, W. In the case of copper, ammoniumthiometallates $CuNH_4M'S_4$ are obtained under analogous conditions [9]. The thermal decomposition of these phases in non-oxidizing atmospheres leads by a topotactic reaction to a microcrystalline intermediate [10] whereas the intermediates of the ammine precursors are amorphous. For the degradation of en-complexes, thermogravimetry as well as X-ray diffraction give no evidence for the existence of an analogous state at all. An interesting and rather specific property of the observed intermediate ternary sulfides is revealed by differential thermal analysis: a distinct exothermal peak appears in a temperature range, where no weight losses are detectable. This phenomenon is explained by a phase segregation process generating the respective binary sulfides MS and $M'S_3$. As final decomposition product, intimate mixtures of the thermodynamically stable sulfides MS_{1-x} and $M'S_2$ are obtained. The mass spectrometric detection of evolved elemental sulfur as well as powder X-ray diffraction confirm these findings. High resolution electron micrographs elucidate a characteristic microstructure made up of intergrown crystalline domains with dimensions in the range of 5 to 10 nm. The degradation of the initial complexes containing the more spacious en ligands leads to mixtures of intergrown binary sulfides with distinctly smaller crystallite sizes [11].

Thermal behavior of delafossite-type ternary and quaternary metal oxides in molecular hydrogen.

Delafossite-type metal oxides ABO_2 are characterized by a highly anisotropic, layered structure, which is made up of linearly coordinated A(I) metals interlinking sheets of edge-sharing $B(III)O_6$ octahedra. The fact that a number of different metal combinations can be stabilized in this structure, e.g. with Cu^+, Ag^+ or Pd^+ occupying the A positions and Fe^{3+}, Cr^{3+}, Al^{3+} or Rh^{3+} in the B positions, renders these phases interesting with respect to physical and chemical properties [12–14]. Moreover, it has been shown that isostructural, quaternary phases with partly substituted A or B cations exist [15]. Delafossites prove to be thermally very stable in inert or oxidizing atmospheres. Under reducing conditions, e.g. in molecular hydrogen, thermal degradation is observed. The nature of the products as well as the reaction temperatures directly depend on the metals present in the initial materials. In order to study a possible metal selective reduction behavior, two combinations comprising metals with highly different properties, i.e. $CuAlO_2$ and $CuRhO_2$, as well as the respective quaternary phases $CuRh_xAl_{1-x}O_2$ $(0<x<1)$ were selected.

Depending on the compositions, the temperature range of the reductions in pure H_2 varies from ≈ 1000K (for pure $CuAlO_2$) to ≈ 450K (for pure $CuRhO_2$). Furthermore, thermogravimetry reveals single step reductions for all compounds. As products, elemental copper, thermally metastable Cu-Rh-alloys and alumina are formed.

The mentioned reactions are of particular interest with respect to the preparation of mixtures of finely dispersed elemental metals or alloys and alumina. Thus, the initial phases represent integrated precursor systems for supported metallic or bimetallic catalysts. Indeed, such materials act as efficient catalysts for e.g. the selective reduction of CO_2 by H_2 to CH_4 at 600K [16].

Conclusions

The given examples demonstrate that thermoanalytical techniques combined with mass spectrometry are most valuable tools for exact studies of the compositional changes occuring in the course of heterogeneous solid state reactions. These techniques, however, are inherently not structure-specific. Nevertheless, the knowledge of structural relationships between initial, intermediate and product phases is indispensable for elucidating reaction mechanisms on a microscopic, i.e. atomic scale. Thus, thermal analysis of reacting solids has to be supplemented by structural investigations. Apart of the chemical composition and the structure the comprehension of 'form' in a wider sense includes also the morphology of solids, which evidently is closely related to the structure. Results obtained by optical as well as scanning and high resolution electron microscopy are important complements for describing solid state reactions and for understanding the interdependence of macroscopic and microscopic reaction mechanisms. High resolution electron microscopic imaging and selected area electron diffraction are of particular value, where, owing to e.g. extremely small particles or domains in multiphasic solid products X-ray diffraction techniques are no more applicable.

Together with energetic criteria, the above mentioned concept represents a promising basis for the controlled modification of specific properties of products phases, e.g. the generation of thermodynamically metastable compounds such as the described ternary metal sulfides or the bimetallic Cu-Rh-alloys. Alternate synthetic pathways do also lead to mono- or multiphasic materials, which may be thermodynamically stable, but as a matter of fact unaccessible by conventional preparative techniques.

In total, a better understanding of the thermochemical reactivity of solids is the prerequisite for the preparation of products exhibiting optimized properties with respect to their applicability in e.g. catalysis or materials science.

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Zusammenfassung — Strukturelle Parameter spielen eine große Rolle beim Ablauf heterogener Festkörperreaktionen. Wegen der engen Beziehungen zwischen Form und Reaktivität fester Stoffe sind detaillierte morphologische Untersuchungen besonders wichtig. Damit können eindeutige Zusammenhänge zwischen dem mikroskopischen Reaktionsmechanismus und den beobachteten makroskopischen Änderungen abgeleitet werden.

Wir interessieren uns zur Zeit besonders für die Herstellung von Feststoffen mit "massgeschneiderten" spezifischen chemischen und physikalischen Eigenschaften. Ausgehend von geeigneten Vorprodukten und bei günstigen experimentellen Bedingungen, insbesondere beim Arbeiten mit reaktiven Gasen, wie molekularem Wasserstoff, wird die kontrollierte Herstellung z.B. von katalytisch aktiven Metallen oder Legierungen sowie binären und ternären Metalloxid- und -sulfidphasen möglich.

Dabei haben sich thermoanalytische Methoden in Kombination mit Massenspektrometrie und Gaschromatographie als unverzichtbar erwiesen.

РЕЗЮМЕ — Установлена роль структурных факторов, затрагивающих ход гетерогенных твердотельных реакций. Вследствии тесной взаимосвязи между формой и реакционной способностью твердых тел, особое внимание должно быть уделено детальным морфологическим исследованиям. Это позволило вывести хорошие корреляции между реакционным механизмом на микроскопическом уровне и наблюдаемыми макроскопичесими изменениями. Главное внимание авторов было сосредоточено на получении твердых тел с "специально приготовленными" специфическими химическими и физическими свойствами. Начиная с выбора подходящих исходных веществ и подбора соответствующих экспериментальных условий, особенно, при работе с такими реакционноспособными газами, как молекулярный водород, проведено контролируемое получение каталитически активных тонко диспергированных металлов или сплавов, наряду с получением двойных и тройных оксидов и сульфидов металлов. При этом, как правило, термоаналитические методы комбинировались с масс-спектрометрией и газовой хроматографией.