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In celebration of the 60^{th} birthday of Dr. Andrew K. Galwey

STRUCTURAL AND MORPHOLOGICAL CHANGES CHARACTERIZING REVERSIBLE DE-AMMINATION/ RE-AMMINATION PROCESSES IN $NiPt(CN)_4(NH_3)_2$

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Abstract

The topotactic structural mechanism of de- and re-ammination of single-crystalline $NiPt(CN)_4(NH_3)_2$ is characterized by means of structural, morphological and thermoanalytical studies. Structural investigations give evidence that the two-dimensional structural motif $[NiPt(CN)_4]_\infty$ determines the mechanism and the kinetics of both processes. It is shown that the degree of reversibility, in particular the exothermic re-ammination, is governed by the conservation of the two-dimensional structural element $[NiPt(CN)_4]_\infty$. Indeed, only one type of bond has to be broken, and reformed, i.e. the two $Ni\text{-}NH_3$ bonds per Ni. Microscopic studies reveal that by starting with single crystals with average dimensions of few tenths of a mm, each cycle of de- and re-ammination leads to a continuous decrease of the size of crystalline domains until an optimum geometry is reached for the given experimental conditions. By semi-quantitative measurements it can be shown that this direction-dependent kinetic course of the overall reaction is controlled by the diffusion of ammonia along the $[NiPt(CN)_4]_\infty$ layers. If the macroscopic size of these layer fragments is very small, i.e. after several cycles of the reversible reaction, this diffusion control becomes negligible. The reaction is controlled by the availability of reactive Ni sites and ammonia, i.e. its partial pressure.

Keywords: heterogeneous solid state reactions, kinetics, $NiPt(CN)_4(NH_3)_2$ and $NiPt(CN)_4$, reversibility, topotactic structural reaction mechanism

Introduction

The importance of heterogeneous solid state reactions arises from the need for controlled preparation of materials exhibiting preferable chemical and physical properties. Specific physical properties are usually achieved by the

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controlled design of structure-composition relations. Structural modifications, compositional substitution, or anion and cation non-stoichiometry may be mentioned as possibilities for controlling one- or more dimensional conductivity properties. Specific chemical properties, in particular the reactivity of solid compounds, do not only afford structure-composition relationships, but also satisfactory morphological features with respect to the desired reaction behaviour. For catalytic activity, a high specific surface may be of importance, for sensor technology access to thin epitactic films, or to compounds with an extreme cation or anion mobility may be useful. Thus, the design of compositionally, structurally and morphologically well-defined materials represents one of the most attractive and competitive fields in modern inorganic chemistry. Many research activities focus on the preparation and transformation of precursor phases, which in turn may be volatile – as used for CVD and MOCVD techniques – or which decompose reproducibly to products with specific properties. Such decomposition processes are often governed by topotactic structural reaction mechanisms. In turn, the structural and morphological properties of a product phase can be controlled by the selection of a parent precursor phase, which decomposes with conservation of structural elements [1–3].

In this study, the reversibility of a highly topotactic heterogeneous solid state reaction is discussed. As parent phase, the solid complex compound $NiPt(CN)_4(NH_3)_2$ has been chosen [4, 5]. It adopts the basic structural framework of the well-known Hofmann-type inclusion compounds $Ni(CN)_2(NH_3)(X)$ with X = benzene, pyrrole, aniline, thiophene, etc. [6–8]. These inclusion compounds have recently become more and more important in the field of supramolecular architecture and its potential for the synthetic control of solids [9]. Owing to rather weak bonding forces between host and inserted compound, the reversible insertion/evolution of the mostly organic molecules does not affect the structural framework. The mechanism and kinetics of insertion are, however, strongly dependent on the morphology of the parent host phase, i.e. the crystal size directly determines the diffusion paths for the molecules being inserted.

The de-ammination and the re-ammination in $NiPt(CN)_4(NH_3)_2$, however, include the breaking or formation of chemical bonds. The question of how these chemical reactions affect the structural framework as well as the morphology of the parent or product phases was tackled by the following experimental investigations. The kinetics of the reversible process are also discussed.

Experimental

Synthesis

$K_2[Pt(CN)_4]\cdot 3H_2O$ (FLUKA, p.a.) is dissolved in distilled water. By adding a stoichiometric amount of $NiCl_2\cdot 6H_2O$ (FLUKA, p.a.) $[NiPt(CN)_4]\cdot nH_2O$ ($n \approx 2$) precipitates as light-blue powder which is isolated by filtration. Single crystals of $NiPt(CN)_4(NH_3)_2$ are obtained by dissolving $[NiPt(CN)_4]\cdot nH_2O$ in dilute aqueous ammonia and subsequent slow evaporation of the solvent at 50°C. After a few days, the pale-violet crystals of $NiPt(CN)_4(NH_3)_2$ can be filtered off, washed with acetone and dried at 50°C.

$NiPt(CN)_4$ is obtained as microcrystalline brown powder by the thermal decomposition of $NiPt(CN)_4(NH_3)_2$ at 250–300°C in an inert gas atmosphere (N_2).

Structural studies

Structural investigations of powder samples have been carried out using an FR 552 Guinier-IV camera (Nonius, Delft, NL) with $CuK_{\alpha 1}$ radiation and a graphite monochromator, as well as a Guinier-Lenné heating camera with CuK_α radiation. The single-crystal structure determination of $NiPt(CN)_4(NH_3)_2$ has been performed using a FACS-1 four-circle diffractometer (Picker Instr., Cleveland, USA) with graphite-monochromated MoK_α radiation. For the determination of the structural reaction mechanism, partly decomposed $NiPt(CN)_4(NH_3)_2$ crystals were investigated by means of a Weissenberg camera (Nonius, Delft, NL) with CuK_α radiation.

Thermoanalytical measurements

The course of the thermal decomposition of $NiPt(CN)_4(NH_3)_2$ has been recorded with a simultaneous thermogravimetry/mass spectrometry unit made up of a TGS-2 thermobalance (Perkin-Elmer, Connecticut, USA) coupled by a heated capillary to a QMG-511 quadrupole mass spectrometer (Balzers, FL). Reaction enthalpies have been measured in inert and reactive gas atmospheres using a DSC-2B (Perkin-Elmer, Connecticut, USA).

Morphological investigations

The morphological changes occurring during the de- and re-ammination of the parent $NiPt(CN)_4(NH_3)_2$ single crystals have been investigated by means of light microscopy and scanning electron microscopy using a Stereoscan S1 microscope (Cambridge Instr., GB).

Results

Structural data

$NiPt(CN)_4(NH_3)_2$ crystallizes with tetragonal symmetry, space group $I4_1/amd$ as bi-capped tetragonal bipyramids. The unit cell parameters are as follows: $a = b = 7.400(1)$ Å, $c = 17.176(4)$ Å, $Z = 2$, $V = 940.56$ Å^3. As Fig. 1a shows, the structure is made up of infinite $[NiPt(CN)_4]$ layers. The square-planar coordination of Pt is made up of $4C_{(CN)}$ and the octahedral coordination of Ni is made up of 4N(CN) and two $N(NH_3)$ in the axial positions. This structure is analogous to $[Ni(CN)_2NH_3]_2$ [10].

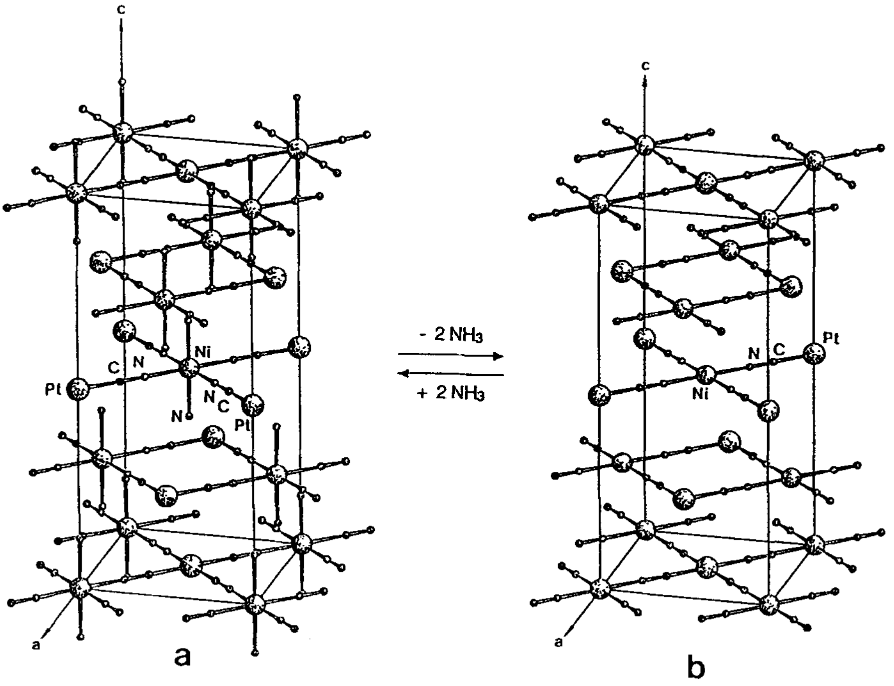

Fig. 1 Schematic representations of the atomic structures of the parent phase $NiPt(CN)_4(NH_3)_2$ (a), and its decomposition product $NiPt(CN)_4$ (b). The structural relationship between the amminated and the de-amminated phases, i.e. the conservation of $[NiPt(CN)_4]_\infty$ layers, explains the highly topotactic and reversible de-ammination/re-ammination process

The structure of $NiPt(CN)_4$ is closely related to the structure of the diammine compound: it is made up of infinite $[NiPt(CN)_4]$ layers, where Ni as well as Pt exhibit square-planar $Ni(CN)_4$ and $Pt(CN)_4$ coordinations (Fig. 1b). From X-ray powder diffraction data, the following unit cell parameters were derived: $a = b = 7.227(5)$ Å, $c = 13.733(24)$ Å, $Z = 4$, $V = 717.27$ Å^3. This compound adopts a structure closely related to that of $Ni(CN)_2$ [11]. As a consequence of the different composition, however, the c-axis is doubled. The distances between the layers (001) are very similar, i.e. 3.44 Å for $NiPt(CN)_4$ and 3.19 Å for $Ni(CN)_2$.

The structural data suggest that de-ammination and re-ammination processes should not affect the $[NiPt(CN)]_\infty$ layers. This statement is supported by the fact that the a-axes of the parent and product phases only differ by 2.4%. The structural changes during the de-ammination can be described as pronounced shrinkage of the c-axis, i.e. the distance between the layers decreases ~25%.

X-ray diffraction investigations, using partly decomposed $NiPt(CN)_4(NH_3)_2$ single crystals, fully confirm this suggestion: the structural mechanism of the de-ammination is governed by the two-dimensional structural element $[NiPt(CN)_4]_\infty$, resulting in a high degree of topotaxy.

Thermoanalytical measurements

Simultaneous thermogravimetric/mass spectrometric measurements showed that, in an inert gas atmosphere (1 bar N_2), $NiPt(CN)_4(NH_3)_2$ decomposes above 250°C to $NiPt(CN)_4$ with evolution of ammonia (Fig. 2). The measured mass loss corresponds to the stoichiometric value. The brown product $NiPt(CN)_4$ is stable in air. No reaction was observed when this phase was exposed to humidity. In water no solubility could be observed. If the sample is exposed to gaseous ammonia at room temperature, however, it immediately undergoes re-ammination. TG measurements of the re-amminated product confirm, that the stoichiometry is fully reached. Attempts to monitor the re-ammination in an ammonia atmosphere within the thermobalance failed, because the reaction time was so short (see below) that reaction was complete before the balance had stabilised after the convection caused by the change of the gas atmosphere. Consequently the de-ammination, as well as the re-ammination, have been measured by means of DSC. In Fig. 3 a series of measurements is presented: Fig. 3a shows the de-ammination of a few $NiPt(CN)_4(NH_3)_2$ single-crystals (typical mass of an isolated single-crystal: ~ 40 μg) in a N_2 atmosphere. The enthalpy change is 130±10 kJ/mol. In Fig. 3b the re-ammination at room temperature is displayed. Note the short reaction time of only ~ 100 sec at a reaction temperature of 70°C! For this process an enthalpy of

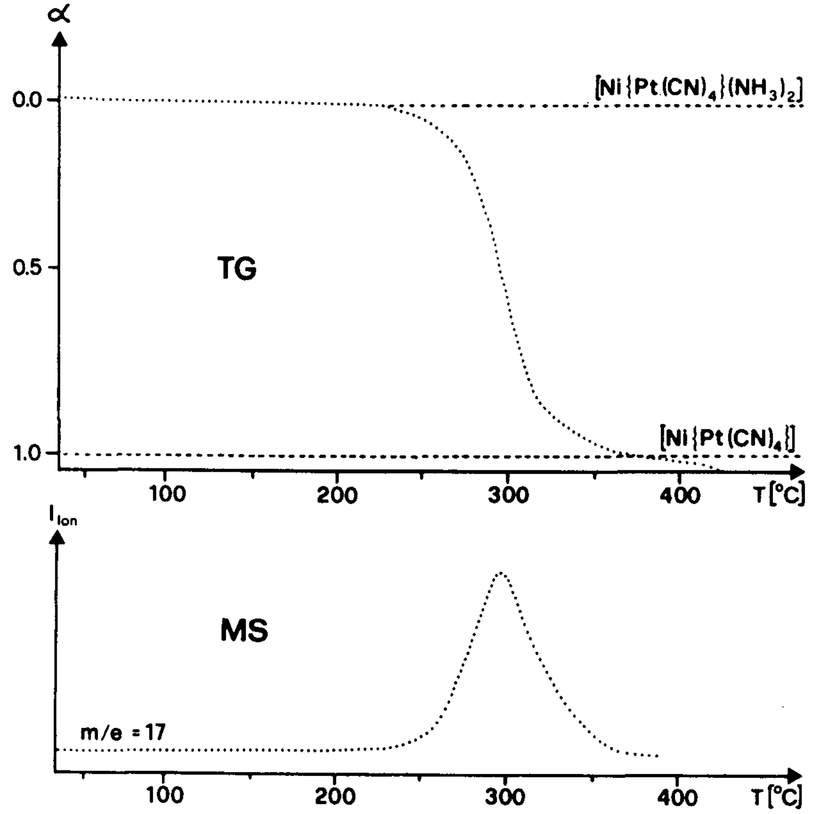

Fig. 2 Simultaneous TG /MS measurement of the thermal decomposition of $NiPt(CN)_4(NH3)_2$ to $NiPt(CN)_4$ (heating rate: 10 deg·min^{-1}; atmosphere: N_2 atmospheric pressure; monitored mass *m/e*: 17)

−135±10 kJ/mol was registered. After ten cycles of de- and re-ammination, a two-step decomposition seems to prevail. This can be explained by the formation of an intermediate $NiPt(CN)_4(NH_3)^*$, i.e. only half of the Ni cations are coordinated to two ammonia molecules, or all Ni cations are coordinated to only one ammonia. A proof for this observation by means of structural data cannot be given. The fact, however, that the temperature of onset of the decomposition remains high confirms the presence of chemically bound ammonia in the re-amminated product. Adsorbed ammonia would be evolved at temperatures below 100°C. This argument is supported by the fact that the measured decomposition enthalpy is 120±10 kJ/mol. Although this value is slightly lower than that for the first decomposition, it still confirms the reversibility of the overall process $NiPt(CN)_4 + 2NH_3 \leftrightarrows NiPt(CN)_4(NH_3)_2$.

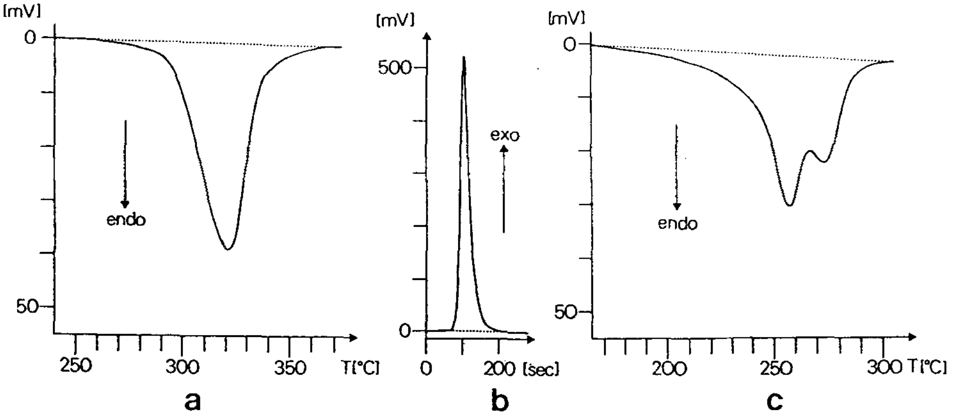

Fig. 3 Dynamic and isothermal DSC measurements of the reversible de-/re-ammination in the system $NiPt(CN)_4(NH_3)_2/NiPt(CN)_4$. In Fig. 3a a DSC measurement of the endothermic decomposition of $NiPt(CN)_4(NH_3)_2$ is presented (heating rate: 5 $deg \cdot min^{-1}$; atmosphere: N_2 enthalpy change: 130±10 kJ/mol). In Fig 3b a DSC measurement of the exothermic process $NiPt(CN)_4+2NH_3 \rightarrow NiPt(CN)_4(NH_3)_2$ is displayed (sample: product of the decoposition process presented in Fig. 3a; isothermal conditions, 70°C; atmosphere: NH_3; ethalpy change: –135±10 kJ/mol). Figure 3c shows the DSC measurement of the endothermic decomposition of $NiPt(CN)_4(NH_3)_2$, which was obtained after ten de- and re-ammination cycles (experimental conditions analogous to the experiment presented in 3a; enthalpy change: 110 kJ/mol)

Morphological studies

Light and scanning microscopic investigations give evidence that the de-ammination of $NiPt(CN)_4(NH_3)_2$ single-crystals leads to perfect $NiPt(CN)_4$ pseudomorphs (Fig. 4). To get insight into the structural mechanism, partly decomposed single-crystals were cut parallel to the $[NiPt(CN)_4]_\infty$ layers. As is shown in Fig. 5, the reaction front moves along the layers into the crystal. There is no sharp parent phase/product phase boundary. Moreover, at the corners of the partly decomposed crystal, the reaction front obviously moves with an even lower velocity. These observations suggest a diffusion-controlled mechanism, where local increases of the ammonia partial pressure – which are to be expected at the corners – decrease the rate of the decomposition, i.e. affect the equilibrium. This argument is supported by the observed reversibility of the overall process. Sections perpendicular to the $[NiPt(CN)_4]_\infty$ layers confirm the highly topotactic structural mechanism. As it is shown schematically in Fig. 6, the macroscopic changes occurring during the decomposition of $NiPt(CN)_4(NH_3)_2$ single crystals can be interpreted as being a direct consequence of the structural mechanism governed by the conservation of the specified two-dimensional structure element.

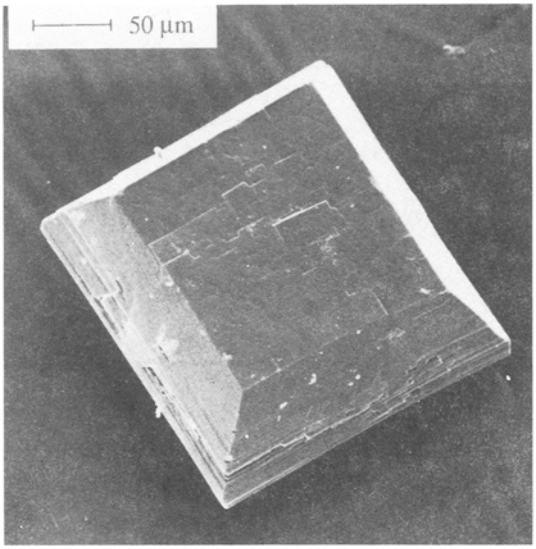

Fig. 4 Scanning electron micrograph of $NiPt(CN)_4$ pseudomorph obtained by the thermal decomposition of a $NiPt(CN)_4(NH_3)_2$ single crystal

Detailed morphological and structural studies by means of SEM and X-ray-diffraction reveal that repeated de- and re-ammination processes result in the formation of pseudomorphs made up of continuously decreasing homogeneously scattering crystalline domains, i.e. decreasing crystallinity (Fig. 7 a–c). After ~10 cycles, however, the crystallinity remains unchanged. Scanning micrographs of such a sample still show a morphology characterised by macroscopic, highly orientated $[NiPt(CN)_4]_\infty$ layers (Fig. 8). Thus, under the given experimental conditions, an optimum size of crystallites for the reversible de- and re-ammination is obtained.

Discussion

The experimentally observed reversibility of the reaction $NiPt(CN)_4 + 2NH_3 \leftrightarrows NiPt(CN)_4(NH_3)_2$ can be explained by the corresponding highly topotactic structural mechanism (Fig. 1): for the decomposition, only Ni–NH_3 bonds have to be broken. Volatile ammonia diffuses along the $[NiPt(CN)_4]_\infty$ layers, but never perpendicular to the layers, to the side surfaces of the macro-

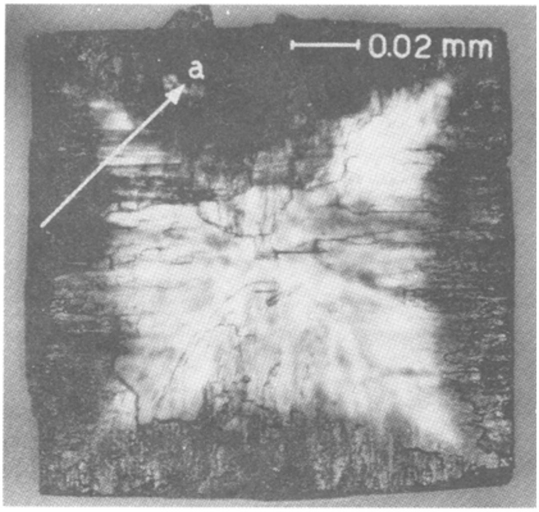

Fig. 5 Light-microscopic image of a partially decomposed $NiPt(CN)_4(NH_3)_2$ single crystal/(section). The dark domains correspond to decomposed material, i.e. $NiPt(CN)_4$, the light central domain to the parent phase $NiPt(CN)_4(NH_3)_2$

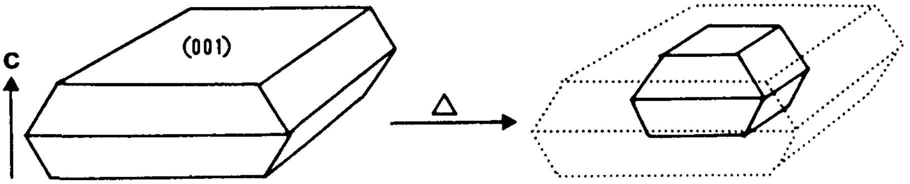

Fig. 6 Scheme for the macroscopic reaction mechanism for the decomposition of a $NiPt(CN)_4(NH_3)_2$ single crystal. The $NiPt(CN)_4(NH_3)_2/NiPt(CN)_4$ reaction front basically proceeds along the $[NiPt(CN)_4]_\infty$ layers, i.e. in the direction perpendicular to [001] of the parent $NiPt(CN)_4(NH_3)_2$ structure. The full lines in the scheme of the partially decomposed single-crystal (right) indicate the shape of the remaining $NiPt(CN)_4(NH_3)_2$, the dotted lines indicate the conserved shape of the $NiPt(CN)_4$ product pseudomorph

scopic crystal (Figs 5 and 6). The change of volume induces mechanical stress leading to the formation of $NiPt(CN)_4$ domains, which are perfectly oriented with respect to the parent structure. Thus, the solid product represents a nearly perfect pseudomorph of the initial single crystal. As a result of this thermal decomposition, the potentially reactive sites, i.e. the axial coordination sites of the Ni, remain unoccupied (see structure of $[NiPt(CN)_4]$ in Fig. 1). At lower temperatures and under a partial pressure of ammonia the reverse reaction takes place and the initial complex is formed again. Consequently the reversibility of

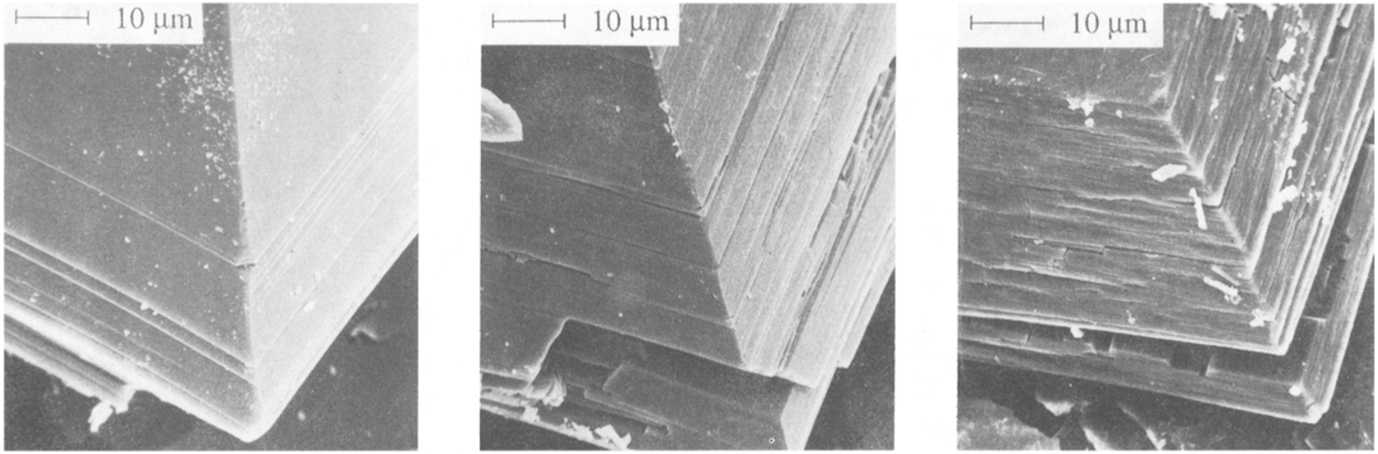

Fig. 7 Scanning electron micrographs of the surface of a $NiPt(CN)_4(NH_3)_2$ single crystal (left), of a decomposed $NiPt(CN)_4(NH_3)_2$ single crystal, i.e. pseudomorphous $NiPt(CN)_4$, and of a $NiPt(CN)_4$ pseudomorph obtained after various (10) de- and re-ammination processes (right)

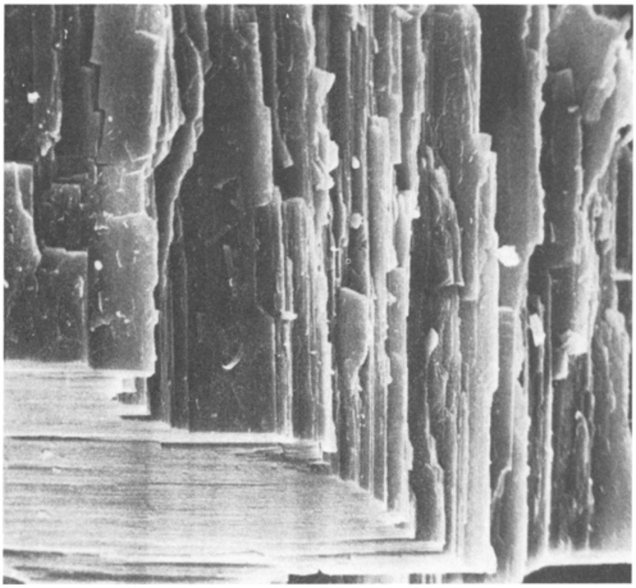

Fig. 8 Scanning electron micrograph of a mechanically broken $NiPt(CN)_4$ pseudomorph. The macroscopic layers correspond to the crystallographic $[NiPt(CN)_4]_\infty$ layers, $(001)_{NiPt(CN)_4(NH_3)_2} // (001)_{NiPt(CN)_4}$

the overall reaction is governed by the two-dimensional topotactic structural mechanism. The de- and re-ammination can be controlled by either the reaction temperature or the ammonia partial pressure: a solid state reaction analogue of a classical equilibrium process in solution or gas phase. However, the question of the rate-determining step is not yet answered. Semi-quantitative measurements using isolated single crystals were carried out. Using a phenomenological approach [12], which is based on the linear or exponentially decreasing movement of the parent phase/product phase boundary along the $NiPt(CN)_4$ layers, it was found that the diffusion of the volatile products is rate determining. Quantitative data for the rate constant k_a, i.e. the number of Ni–NH_3 bond breaks along the crystallographic a–axis as function of temperature, pressure and distance to the surface of the macroscopic crystal, could not be determined. The available single crystals of the parent phase $NiPt(CN)_4(NH_3)_2$ were too small (~$0.3\times0.3\times0.15$ mm^3 according weight: ~40 μg, corresponding mass changes: ~4 μg).

Conclusions

Solid coordination compounds represent very suitable systems for studies on the mechanisms and kinetics of heterogeneous solid-state reactions. Owing to the vast spectrum of parent structural motifs and frameworks, as well as variable ligands, the interdependent course of the microscopic and macroscopic reaction mechanisms can be sorted out by reaction rate dependent structure/morphology studies. In the case of highly topotactic reactions, the energetic course with respect to the bonds being broken or formed can be unravelled. For the reaction described, $NiPt(CN)_4(NH_3)_2 \leftrightarrows NiPt(CN)_4 + 2NH_3$, the structural reaction mechanism allows a nearly perfect reversibility. Three main arguments may be derived from these observations:

– The determination of the mechanisms and kinetics of heterogeneous solid-state reactions permits the characterization of qualitative structural and compositional changes. Based on the known structural mechanisms, as well as structure/morphology relations, the measurement of the time and temperature dependent course of the reaction allows the quantitative measurement of specific rate constants. In contrast to rate constants of reactions in the liquid or gaseous phase, such constants include a structural or directional component which refers to the structural mechanism.

– The knowledge of the energetics of heterogeneous solid-state reactions, i.e. which types of bonds are broken or formed under a given energetic or chemical potential, can be used for the design of processes – as demonstrated by the described reversibility of de- and re-ammination – or for the design of precursor systems which can be decomposed to tailor-made solids. The presented reversible reaction is considered as a model for an ammonia storage system. As an essential prerequisite of such a system, the back-reaction needs to be exothermic, i.e. the reaction sites for the ammonia immobilization need to remain accessible in terms of energetic, structural and morphological features.

– The possibility of designing appropriate precursor systems and decomposition processes represents a good basis for the generation of solids exhibiting tailor-made textures and morphologies, i.e. exhibiting a 'Realstruktur' with desired properties.

These arguments emphasize the needs for research activities in the field of materials science and development. The increasing importance of inorganic solids as heterogeneous catalysts, components of high-tech facilities, or constituents of composite materials presents a real challenge to the understanding of heterogeneous solid state reactions.

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Zusammenfassung — Mittels Struktur-, morphologischen und thermoanalytischen Methoden wurde der topotaktisch-strukturelle Mechanismus der De- und Reamminierung von $NiPt(CN)_4(NH_3)_2$-Einkristallen untersucht. Die Strukturuntersuchungen machten deutlich, daß das zweidimensionale Sturkturmuster $[NiPt(CN)_4]_\infty$ Mechanismus und Kinetik beider Prozesse bestimmt. Es wurde gezeigt, daß der Grad der Reversibilität, insbesondere die exotherme Reamminierung von der Konservierung des zweidimensionalen Strukturelementes $[NiPt(CN)_4]_\infty$ beherrscht wird. Es braucht nur eine Art von Bindungen gespalten und wieder geschlossen zu werden, nämlich die zwei Ni-NH_3 Bindungen pro Ni-Atom. Mikroskopieuntersuchungen ergaben, daß - ausgehend von Einkristallen mit durchschnittlichen Dimensionen von einigen Zehntel Millimeter - jeder De- und Reamminierungszyklus zu einem stetigen Anwachsen des kristallinen Weißschen Bezirkes führt, bis für die gegebenen experimentellen Bedingungen eine optimale Geometrie erreicht wurde. Durch semiquantitative Messungen konnte gezeigt werden, daß dieser richtungsabhängige kinetische Verlauf der Gesamtreaktion durch die Diffusion von Ammoniak entlang der $[NiPt(CN)_4]_\infty$ Schichten kontrolliert wird. Sind diese Schichtfragmente makroskopisch gesehen sehr klein, d.h. nach einigen Zyklen der reversiblen Reaktion, wird diese Diffusionskontrolle vernachlässigbar. Die Reaktion wird durch die Verfügbarkeit reaktionsfähiger Ni-Stellen und durch den partiellen Druck von Ammoniak bestimmt.