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KINETIC STUDY OF THE SOLID PHASE REACTION OF AMMONIUM NITRATE AND COPPER OXIDE BY THE USE OF FAST X-RAY DIFFRACTION

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The solid state reaction of ammonium nitrate and copper oxide was studied by the use of energy dispersive and angle dispersive x-ray diffraction. The reaction takes place within the temperature interval 110 to 150 °C and consists of two steps. The product of these consecutive reactions is the diammine copper complex. The relative concentrations of the species involved were evaluated by summing up difference x-ray spectra. The resulting curves were analyzed by a computer program to obtain the kinetic constants of the reactions.

The doping of ammonium nitrate with small amounts of diammine metal complexes influences significantly its phase transitions [1]. The complexes can be prepared by a solid state reaction of the metal oxide with ammonium nitrate [2,3], which requires the knowledge of the reaction kinetics. In addition to the methods of thermal analysis, x-ray diffraction provides a convenient way to study solid state reactions [3]. Thermal analysis by x-ray diffraction uses a heatable sample cell and fast detectors for a fast recording of the diffraction pattern. We used the energy dispersive x-ray diffraction (EDXRD) with a Si(Li) solid state detector (see Giessen and Gordon [4] and Buras et al. [5]) and angle dispersive diffraction with a position sensitive proportional counter (PSPC) [6]. These methods allow a relatively fast acquisition of x-ray spectra during heating experiments with heating rates comparable to that of DTA and TG.

In this paper we investigated the reaction of ammonium nitrate and copper oxide in closer detail. Main interest was focussed on the kinetics of the reaction in order to get reliable data for the phase stabilisation process.

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Experimental

The experimental setup consisted of an x-ray diffractometer (Siemens D 500) and a heating device (TTK of Paar, Graz). For EDXRD a tungsten x-ray tube and Si(Li) detector and for angle dispersive diffraction a chromium tube with a position sensitive proportional counter were used. A microprocessor based programmable temperature controller performed the selected temperature programs, and a PC coordinated temperature control, acquisition of the x-ray patterns in the MCA and the data transfer to a central computer. The block diagram of the angle dispersive system is depicted in fig. 1.

Mixtures of ammonium nitrate (AN) and CuO in molar ratios of 2:1, 4:1 and 8:1 were heated linearly from 20-180 °C with heating rates of 0.5 °C/min or kept at temperatures between 110 and 140 °C in isothermal experiments.

The patterns were obtained by EDXRD below 130 °C and by angle dispersive diffraction at higher temperatures. Series of up to 300 patterns could be measured, each diagram acquired in 200 sec or less.

In addition, TG (Mettler) and DSC (Dupont) curves were recorded with heating rates of 0.5 °C/min.

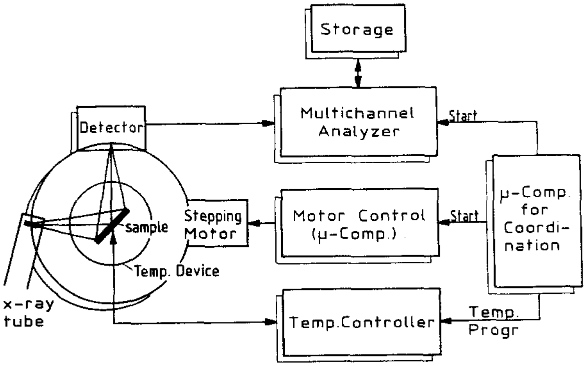

Fig. 1: Block diagram of the angle dispersive x-ray diffraction system with the position sensitive proportional counter

Results and discussion

Fig. 2 shows some angle dispersive x-ray patterns of a series of diagrams obtained during linear heating of a mixture of AN and CuO with a molar ratio of 2:1. The pattern at the bottom of the plot was measured at 20 ^{o}C. It contains the peaks of CuO and AN, phase IV, indicating no interaction. On heating, phase IV changes into phase II at 52-56 ^{o}C, whereas the CuO peaks remain unchanged. The second pattern shows the phase II peaks immediately before the solid state reaction, which begins at 110^{o}C.

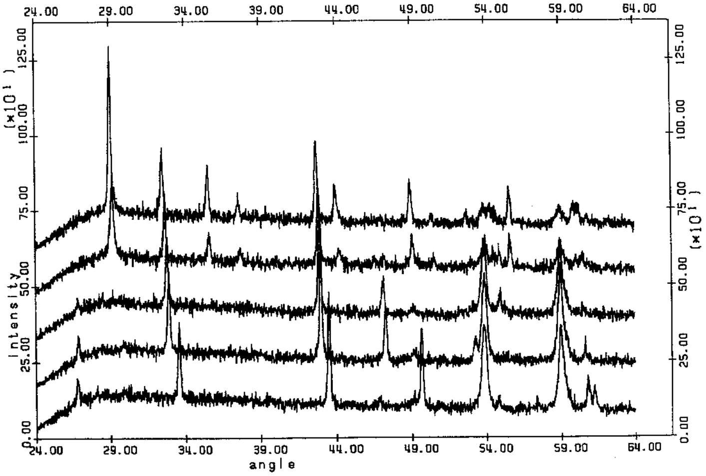

Fig. 2: Series of x-ray patterns obtained during linear heating of ammoniumn nitrate and copper oxide by the use of angle- dispersive x-ray diffraction

The solid state reaction of AN and CuO, shown in the further diagrams, proceeds as follows (peak shifts from isothermal experiments):

1. The peaks of CuO and of $(001)_{II}$ and $(200)_{II}$ of AN decrease.
2. The lattice plane distance of $(110)_{II}$ of AN expands by about 1.5 pm and that of $(111)_{II}$ of AN shrinks first by 2.2 pm and expands then by 0.8 pm. Both peaks reflect during the total reaction, but their intensity is reduced to 90%.
3. At an angle of 55^{o} (0.249 nm lattice plane distance) one peak appears, which splits up into two in the further reaction.

4. A peak at 56° (0.246 nm) shifts immediately after appearance by about 1 pm and then slowly by 0.2 pm to lower distances during the further reaction.
5. Product peaks appear at 29° (0.455 nm), 35° (0.375 nm), 45° (0.305 nm) and 49° (0.276 nm) with a time lag.

The last pattern at the top of fig. 2 is identical with the pattern of diammine copper nitrate above 100 °C produced according to Brauer [7].

Corresponding DSC and TG curves show the endothermic nature of the reaction and a weight loss of about 7% within the reaction interval of 110-150 °C.

Therefore we concluded that AN and CuO react to the diammine complex via a solid state reaction water being the other reaction product, which escapes as observed by the TG:

$$2\ NH_4NO_3 + CuO \ \text{--->}\ [Cu(NH_3)_2](NO_3)_2 + H_2O$$

The reaction occurs by two steps. This is indicated by the time lag between the disappearance of the CuO- and some AN-peaks and the appearance of the product peaks. The most intensive peaks of AN phase II remain nearly unchanged and coincide with peaks of the complex. This implies that the AN lattice planes exist throughout the reaction. The reaction occurs by the diffusion of H^+ out of and Cu^{++} into the lattice accompanied by a small deformation. An intermediate can be identified by the stable position of the AN-peaks and by the peak at 55° (0.249 nm) splitting up, when the reaction continues.
The relationship of phase II to the complex obviously results in a stabilisation of this phase by the complex.

Data evaluation

For a kinetic evaluation it is assumed that the peak intensities are proportional to the concentrations of the interacting species. These are normally obtained by a peak profile fit with the peak intensity, width and position being the fit parameters [3]. In contrast, we used a method of summing up the difference patterns calculated from neighboured (XRTA) or from the first and the actual diagrams (XRDTA) [3].

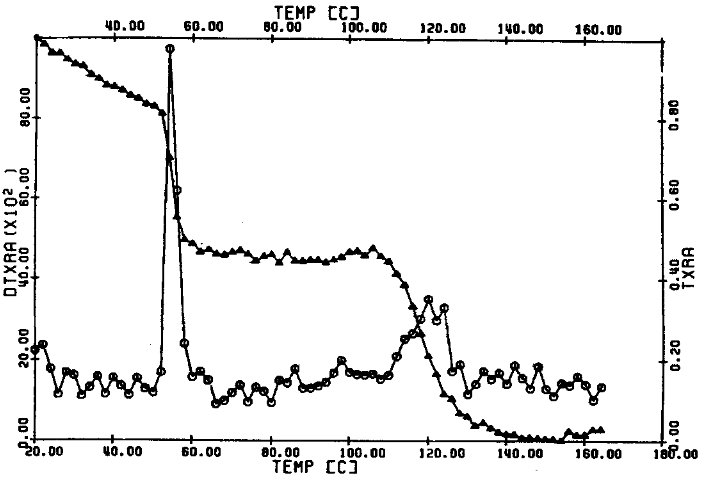

Fig. 3: DTXRA- and TXRA-curves of the series of x-ray patterns

The resulting sums plotted versus time or temperature form a curve similar TG or DTA, respectively. If this evaluation is applied to the region of a single peak the curve quantitatively represents the peak shift or peak intensity change (details see ref. [3]). In the case of small peaks this new type of data evaluation yields more reliable results than peak fitting procedures. This is especially important at the onset or the end of a reaction, where peaks begin to appear or disappear. Compared to peak fitting procedures smoother curves are obtained.

The method was applied to a series of diagrams obtained on linear heating a sample of a molar ratio of 2:1. It results in a curve plotted in fig. 3. The phase transition IV -> II of AN causes a sharp peak (XRDTA) or a steep step (XRTA). The solid state reaction is observed by a broad asymetrical peak or a sigmaoid decay, respectively, from 110 to 150 °C. The curves with molar ratios of 4:1, 8:1 show an increased step at the phase transition and a reduced one at the solid state reaction. This agrees with the diammine copper nitrate being the reaction product.

Isothermal experiments were used to evaluate the kinetics of the reaction. Fig. 4 shows an example of three curves obtained from different regions of the x-ray patterns. As the strongest peaks of AN

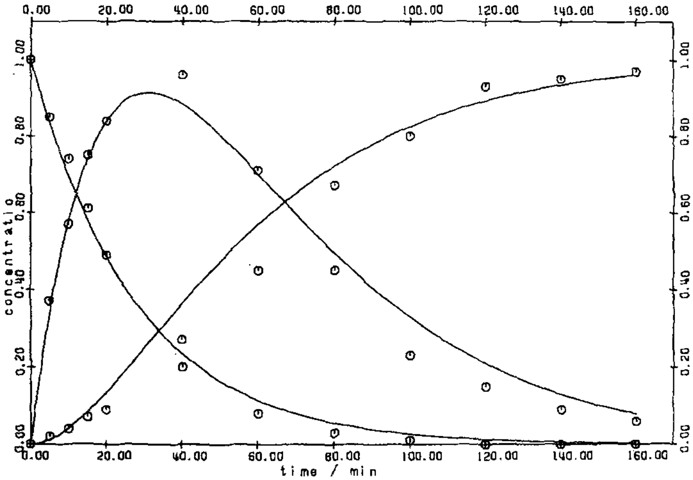

Fig. 4: Experimental data of the concentrations of the reacting components A, B and C and the calculated curves of a two step reaction (temperature 130 °C)

remain nearly unchanged throughout the total reaction, the strong CuO peaks at 54° and 59° were used to represent the starting compound (A). The method applied to the angles between 54.5 and 55.5 ° results in a curve typical for an intermediate (B). The peaks of the diammine complex (C) appear delayed. This is similar to the non-isothermal curves and supports the assumption of a consecutive reaction with the two reaction constants k_1 and k_2:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

The reactions were assumed to be of first order. This assumption allows an easy analytical integration of the reaction equations resulting in the following equations:

$$A = \exp(-k_1 t)$$

$$B = (\exp(-k_1 t) - \exp(-k_2 t))\, k_1/(k_2 - k_1)$$

$$C = 1 + \exp(-k_2 t)\, k_1/(k_2 - k_1) - \exp(-k_1 t)\, k_2/(k_2 - k_1)$$

The solid lines in fig. 4 are the calculated curves A, B and C. They were obtained from a non-linear least squares fit procedure (according to Powell [8]) of the theoretical curves to the experimental ones. All experimental data (A, B and C) were normalized to 1.

Fig. 5 represents the Arrhenius plots of the constants k_1 and k_2. The parameters logarithm of pre-exponential and activation energies are 12.7 ± 1.6 and 123.7 ± 11.7 kJ/mole for k_1 and 9.7 ± 1.1 and 99.9 ± 8.3 kJ/mole for k_2.

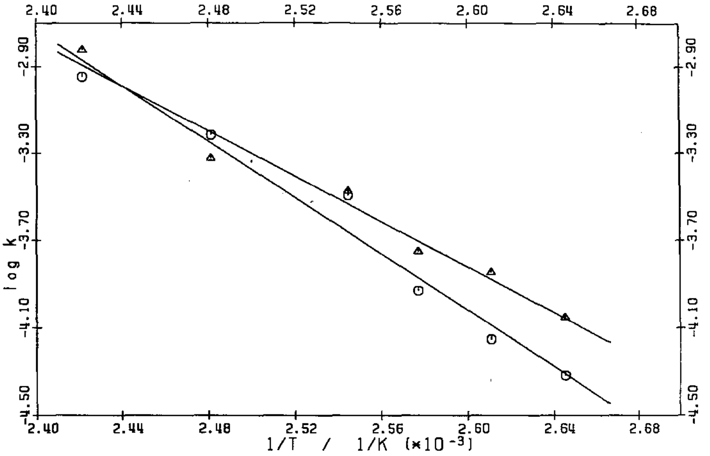

Fig. 5: Arrhenius plot of the reaction constants of the two reaction steps obtained from the least squares fit.

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Zusammenfassung - Mittels Röntgendiffraktionsverfahren wurde die **Feststoff**reaktion von Ammoniumnitrat mit Kupferoxid untersucht. Die Reaktion verläuft im Temperaturbereich 110-150°C und besteht aus zwei Schritten. Das Produkt dieser Folgereaktionen ist der Diamminkupferkomplex. Die relative Konzentration der daran beteiligten Spezies wurde durch Aufsummieren von Röntgendifferenzspektren ermittelt. Anhand der resultierenden Kurven wurden die kinetischen Konstanten der Reaktionen mittels eines Rechnerprogrammes bestimmt.

Резюме - Методом рентгеновской диффракции с рассеянием по энергии и угловым рассеянием изучена твердотельная реакция нитрата аммония с окисью меди. Реакция протекает в две стадии в интервале температур 110-150°. Продуктом реакции является диамминный комплекс меди. Относительные концентрации содержащихся продуктов были оценены суммированием различных рентгеновских спектров. Суммарные кривые затем анализировались с помощью компьютерной программы для получения кинетических констант реакций.