SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Reaction of Zinc Oxide with Ammonium Chloride

V. A. Borisov, A. N. D'yachenko, and R. I. Kraidenko

Tomsk Polytechnical University, pr. Lenina 30, Tomsk, 634050 Russia Received July 20, 2009

Abstract—The reaction of ammonium chloride with zinc oxide was studied kinetically and thermogravimetrically. Reaction products were identified by IR spectroscopy and X-ray powder diffraction. Ammonium chlorozincates were found to form in the reaction and to decompose to zinc chloride.

DOI: 10.1134/S0036023612040043

It is known that ammonium chlorozincates $(NH_4)_2ZnCl_4$ and $(NH_4)_3ZnCl_5$ can be prepared from aqueous solutions containing zinc and ammonium chlorides [1]. Ammonium chloride reacts with metal oxides to form metal chlorides [2]. The reaction of zinc oxide with excess ammonium chlorides yields products that differ from zinc chloride in their physic-ochemical properties [3, 4]. The reaction of zinc oxide with ammonium chloride was suggested to produce ammonium chlorozincates.

The objective of this work is to establish the mechanism of the reaction of zinc oxide with solid ammonium chloride and to identify reaction products.

EXPERIMENTAL

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a combined TGA/DSC/DTA SDT Q600 analyzer with TA Instruments Universal V4.2E software data processing (scale sensitivity, 0.1 µg; DSC noise, $\leq 4 \mu$ W). Studies were conducted within a temperature range of 20–600°C in an atmospheric air flow at a heating rate of 5 K/min in alumina crucibles. A mixture of ZnO (0.50 g) and NH₄Cl (3.30 g) was used for analysis. The sample weight was 20 mg.

Kinetic experiment was conducted by continuous weighing a reaction mixture with automatic mass recording. The conversion was determined from the mass loss due to the formation of gaseous compounds. The ammonium chloride decomposition rate was determined experimentally beforehand at the same temperatures, and the final results were appropriately corrected. The temperature was maintained with an accuracy of ± 2 K. In the kinetic experiment, we used a carefully weighed mixture of zinc oxide and a twofold excess of ammonium chloride with respect to stoichiometry, assuming the formation of zinc chloride, ammonia, and water.

Products of the reaction of ammonium chloride with zinc oxide were synthesized as follows. A mixture of zinc oxide (5.46 g) with ammonium chloride (18.04 g) was sintered in a muffle furnace preheated to 210° C for 12 h. The theoretical composition of the product is $(NH_4)_3$ ZnCl₅.

Elemental analysis was performed as follows. The chloride ion was determined titrimetrically with an AgNO₃ standard solution in the presence of KCrO₄ as an indicator. The studied compound was analyzed for zinc complexometrically. A zinc compound solution was titrated with EDTA in the presence of dithizone as an indicator in aqueous acetone. The ammonium ion was determined photometrically from the absorbance of a colored ammonium complex of Nessler's reagent.

IR spectra were recorded on a Nicolet 6700 Fourier-transform spectrometer (Thermo Electron) within a wavenumber range of $50-4000 \text{ cm}^{-1}$ in nitrogen flow (the ultimate admissible wavenumber scale error was $\pm 0.5 \text{ cm}^{-1}$). For the region 400–4000 cm⁻¹, samples pellets of the studied compound compacted with KBr in the ratio 1 : 300; in the region of $50-400 \text{ cm}^{-1}$, test samples were Nujol mulls.

X-ray powder diffraction analysis was conducted on a DRON-3M diffractometer with a copper anticathode (I = 25 mA, V = 335 kV).



Fig. 1. (1) TGA and (2) DSC curves for the reaction of ZnO with NH_4Cl .



Fig. 2. IR spectrum of the NH₄Cl–ZnO reaction product.

RESULTS AND DISCUSSION

According to TGA data, the heating of a carefully weighed mixture of ammonium chloride and zinc(II) oxide initiates at 150°C the reaction of NH₄Cl and ZnO with the formation of chlorine-containing zinc compound. At 195°C, ammonium chloride begins to decompose with the liberation of gaseous ammonia and hydrochloric acid [5]. Excess ammonium chloride is sublimed at 290°C. A chlorine-containing product is decomposed in steps (Fig. 1) and, at T > 307°C, presumably gives (NH₄)₂ZnCl₄, which in turn decomposes to zinc chloride as follows

$$ZnO + NH_4Cl$$

$$\xrightarrow{150^{\circ}C} (NH_4)_2 ZnCl_4 \xrightarrow{heating} ZnCl_2.$$

The analysis of DSC curves shows that the endotherm associated with the dissociation of ammonium chloride is overlapped by the exotherm (195°C) of the reaction, which evolves into the endotherm (208°C) of the vaporization of gaseous reaction products (H₂O and NH₃). On the whole, the process proceeds with the absorption of heat.

To identify chlorine-containing zinc products, we conducted the solid-phase sintering of ammonium chloride with zinc(II) oxide at 210° C in excess NH₄Cl. The product was studied by IR spectroscopy.

The IR spectrum of a ZnO–NH₄Cl reaction product (Fig. 2) contains absorption bands typical of the $[NH_4]^+$ ion and ammonium chloride at 3270, 3000, 2800, and 1400 cm⁻¹. The bands at 3550 and 1609 cm⁻¹ relate to the bonds of crystal water. The absorption bands at 669, 295, and 140 cm⁻¹, which are typical of



Fig. 3. Conversion vs time for the reaction of ZnO with NH_4Cl .

the M–Cl bond [6], were also found in the IR spectrum of a $ZnO-NH_4Cl$ reaction product.

Relying on the IR spectrum of a chlorine-containing zinc product, we may suppose the presence of free ammonium chloride, which may be due to the use of excessive NH_4Cl in the synthesis, an ammonium complex, and zinc chloride. To unambiguously identify the composition of reaction products, we additionally chemical and X-ray powder diffraction analyses.

According to the results of chemical analysis of the chlorine-containing zinc product (Table 1), the ratio $\text{Zn}: \text{Cl}^-: \text{NH}_4$ is 1: 4.4: 2.4. This indicates the presence of excess ammonia. The presence of excess ammonium chloride in the product allows us to conclude that the chlorine-containing product represents a mixture of zinc chloride or ammonium chlorozincate with ammonium chloride and is not zinc ammoniate.

The X-ray diffraction pattern of the $ZnO-NH_4Cl$ reaction product (Table 2) indicates that ammonium tetrachlorozincate $(NH_4)_2[ZnCl_4]$ and ammonium pentachlorozincate $(NH_4)_3[ZnCl_5]$ are the major components [7, 8].

Table 1. Chemical analysis of the NH₄Cl–ZnO reaction product

	Zn : Cl : NH ₄ ratio	Content, %			
		Zn	Cl	$\rm NH_4$	
NH ₄ Cl–ZnO reaction product	1:4.4:2.4	24.50	58.95	16.55	

REACTION OF ZINC OXIDE

$(ZnO + NH_4Cl)$ sample		(NH ₄) ₂ ZnCl ₄ [12-0304]*		(NH ₄) ₃ ZnCl ₅ [30-0069]**	
<i>d</i> , Å	I, %	$d, \mathrm{\AA}$	<i>I</i> , %	d, Å	I, %
7.8115	19			7.7859	45
6.286	40	6.2752	11		
5.8203	33			5.8104	74
5.1957	100	5.1938	99		
4.9404	21			4.949	50
4.6407	32	4.6437	35		
4.2348	17	4.2336	11		
3.8736	19			3.8782	50
3.6262	31	3.6429	30		
3.2506	23	3.2527	20		
3.1529	65	3.1624	20		
3.0017	43	3.0025	25		
2.8993	23			2.9052	50
2.7694	62	2.7773	59		
2.6346	18			2.6341	15
2.5922	22	2.5969	15		
2.3595	18	2.3599	13		
2.2988	25	2.3029	13		
1.9527	22	1.1.9561	7		
1.882	20	1.8856	9		
1.8168	19	1.8856	9		
1.7971	17	1.8054	7		
1.7678	17	1.7715	5		

Table 2.	X-ray powder	diffraction d	lata for the	NH ₄ Cl–ZnO	D reaction product
----------	--------------	---------------	--------------	------------------------	--------------------

* Powder Diffraction File II, Swarthmore. de Wolff P. Technisch Physische. Dienst. Delft. The Netherlands. ICDD Grant-in-Aid. ** Powder Diffraction File II, Swarthmore. Natl. Bur. Stand. (U.S.) Monogr. 25 15 12 (1978).

Kinetic Studies of the Reaction of Ammonium Chloride with Zinc(II) Oxide

Processing kinetic data on the reaction of zinc oxide with ammonium chloride was carried out using Gistling's, squeezing sphere, and Jander's equations. The applicability of these equations was evaluated by the maximum correlation coefficient $k = f(\alpha, \tau)$.

Experimental data (Fig. 3) were processed by the squeezing sphere equation (correlation coefficients were 0.95-0.98). The following dependence of the conversion α on time τ and temperature *T* was derived:

$$\alpha = 1 - \left(1 - 1.29e^{\frac{-42500}{8.31T}\tau}\right)^3.$$

The process activation energy was 42.5 kJ/mol. The limiting stage was the chemical reaction rate.

Relying on the experimental data, we may say that the reaction of ammonium chloride with zinc(II) oxide begins at 150°C. The reaction mechanism is stagewise and proceeds through the formation of thermally decomposable ammonium chlorozincates $(NH_4)_2[ZnCl_4]$ and $(NH_4)_3[ZnCl_5]$, and zinc chloride is the final reaction product. A way of intensifying the reaction of NH_4Cl with ZnO is to increase the process temperature.

REFERENCES

- 1. Shigera Obba, Acta Crystallogr., Sect. C 43, 189 (1987).
- R. C. Young and J. L. Hastings, J. Am. Chem. Soc. 59, 765 (1937).
- 3. Yu. V. Karyakin and I. I. Angelov, *Pure Chemicals* (Khimiya, Moscow, 1974) [in Russian].
- 4. A. A. Furman, *Inorganic Chlorides* (Khimiya, Moscow, 1980) [in Russian].
- 5. B. D. Mel'nik and E. B. Mel'nikov, *Concise Engineer's Engeer's Hanbook on Technology of Inorganic Materials* (Khimiya, Moscow, 1968) [in Russian].
- K.Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds (Interscience, New York, 1986).
- W. Lang, H. A. Farach, R. J. Creswick, and C. P. Poole, Jr., Phys. Rev. B: Condens. Matter 57 (14), 8155 (1998).
- Z. S. Liu, M. Punkkinen, A. H. Vuorimäki, and E. E. Ylinen, Physica B: Condens. Matter 202 (1994).