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Studies on the thermal behavior of ammonium permanganate

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Abstract

The thermal decomposition of ammonium permanganate was studied by thermogravimetry-mass spectrometry (TG-MS). A Perkin Elmer TGS-2 thermobalance and a Hiden's HAL 3F/PIC mass spectrometer equipped with a fast ion counter was used.

Products of thermal decomposition of ammonium permanganate are oxygen, manganese oxides, water and ammonia. There is no gas phase oxidation of ammonia by oxygen. The possible intermediates of low-temperature decomposition reaction are ammonium nitrite or nitrate which transform into N_2, N_2O, or H_2O. The oxidation of adsorbed ammonia by manganese oxides via the superoxide active centers takes place on the surface of manganese oxide.

Keywords: Ammonium permanganate; Thermal decomposition; Thermogravimetry-mass spectrometry; Ammonia oxidation

1. Introduction

Ammonium permanganate and the products of its thermal decomposition are widely used as oxidants or catalysts in material technology [1].

The thermal decomposition of ammonium permanganate was investigated by many authors. Bircusmhaw and Taylor have studied the kinetics of decomposition of this salt under oil [2]. The kinetics and mechanism of decomposition under vacuum were performed by Pavlyuchenko et al. [3]. The effect of UV irradiation [4] and of ultrasonic initiation [5] on the thermal behavior of ammonium permanganate, as well as the composition of solid phase under thermal treatment were also studied [6].

Although all the authors have defined the chemical composition of evolved gases under thermal decomposition of ammonium permanganate, the relationship between the composition of the gas phase and the temperature ranges belonging to the degradation steps has not been studied yet. The mechanism of formation of some unusual gaseous reaction products e.g., N_2O has not been determined either.

2. Experimental

Ammonium permanganate was prepared from barium manganate and ammonium sulphate [7]. The

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product was recrystallized from water and dried in the dark.

The thermal decomposition of the sample was studied by thermogravimetry-mass spectrometry (TG-MS). This computerized atmospheric pressure thermobalance-mass spectrometer (TG-MS) system had been built of a Perkin Elmer TGS-2 thermobalance and a Hiden's HAL 3F/PIC mass spectrometer equipped with a fast ion counter. Small amounts of samples (0.72 mg) were heated from 20°C at a heating rate of 1°C min^{-1} in a platinum sample pan. The surface of the sample was covered with a layer of high purity Al_2O_3 (1 mg) to prevent the explosion-like degradation of NH_4MnO_4. The ambient gas was high purity argon with a flow rate of 140 ml min^{-1}. The evolved gases were led from the sample pan to the mass spectrometer through a heated capillary within approximately 1 s. A small portion of the carrier gas was introduced into the ion source of mass spectrometer through a molecular hole. The ion source was operated at 70 eV electron energy. Selected mass spectrometric intensities were measured as functions of temperature. The mass spectrometric intensities were normalized by the initial sample mass and by the sensitivity factors calculated from the observed isotope intensity ($^{38}Ar^+$) of the ambient gas. The DTG curves were calculated by spline smoothing. The performance of the system was checked by measuring the three decomposition steps of calcium oxalate monohydrate [8].

3. Results and discussion

During the thermal decomposition of ammonium permanganate ammonia releases and the destruction of anion provides manganese oxides besides oxygen evolution. The oxidation reactions of ammonia or ammonium ion resulting in the formation of water and nitrogen containing oxidation products (e.g. elementary nitrogen or nitrogen oxides and ammoninum nitrate) can also be observed [1–6].

All possibilities of fragmentation pathways were taken into consideration at the same time in order to distinguish the species with identical masses.

Nitrogen containing oxidation products can be formed in two ways: via oxidation of ammonium ion or retained ammonia in solid phase; or in further oxidation or ignition of previously formed ammonia in gas phase. The presumed oxidation agents of these reactions are permanganate ion, oxygen or primary reaction products having higher oxidation states as the higher valence manganese oxides, nitrogen oxides or transition unstable ions (e.g. as superoxide ion). Catalytic effects of reaction products (e.g. manganese oxides) cannot be excluded in the entire decomposition processes.

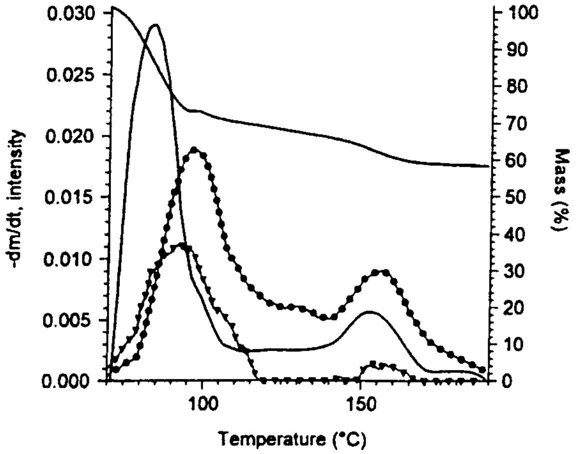

Fig. 1. Comparison of TG, DTG and ion intensity curves of H_2O and O_2 (m/z 18: -●- and m/z 32: -▼, respectively) during the thermal decomposition of NH_4MnO_4. (Ion intensity curves are in arbitrary scales.)

Figs. 1–3 show the gaseous thermal decomposition products of ammonium permanganate. Table 1 lists

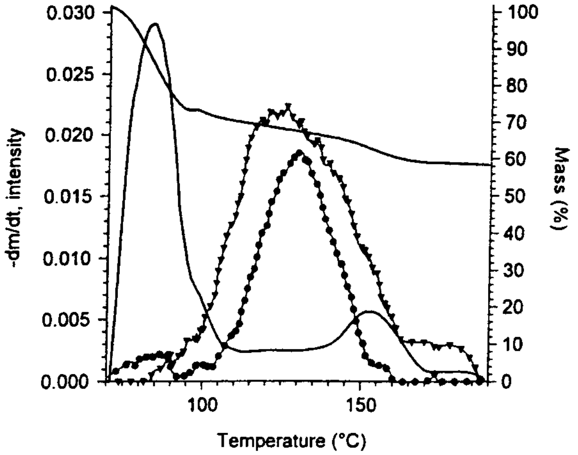

Fig. 2. Comparison of TG, DTG and ion intensity curves of NH_2^+ and NH_3 (m/z 16: -●- and m/z 17: -▼-, respectively). (Ion intensity curves are in arbitrary scales).

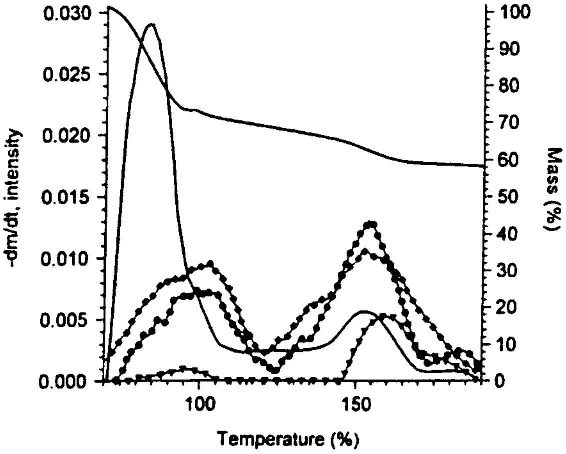

Fig. 3. Comparison of TG, DTG and ion intensity curves of N_2, NO^+ and N_2O (m/z 28: -●-, m/z 30: -▼- and m/z 44: -◆-, respectively). (Ion intensity curves are in arbitrary scales).

data of the maximum mass spectrometric ion intensity values and temperature regions belonged to the ion curves.

3.1. On the decomposition reaction of NH_4MnO_4

The heat transfer among ammonium permanganate crystals plays an important role in the rate of decomposition [2,9], thus the high reaction heat causes a fast overheating of each site of crystals. As it can be seen from Table 1 and from Figs. 1 and 2 the decomposition starts below 70°C and becomes very quick at around 85°C. The main step is the simple decomposition reaction with formation of ammonia, oxygen and water. The permanganate anion totally decomposes in this temperature interval, thus above 115°C the amount of formed oxygen is negligible.

$$2NH_4MnO_4 = 2NH_3 + H_2O + 2MnO_2 + 1.5O_2 \qquad (1)$$

As can be seen from Eq. (1), the water is not an oxidation product of ammonia.

It is known [3] that the presence of ammonia and water decreases and the presence of oxidants (e.g. oxygen) increases the rate of decomposition. Based on the formation profiles of ammonia and oxygen we can state that the evolution of ammonia and oxygen starts at the same time. The autocatalytic character of this reaction is complex due to the presence of many active species as manganese oxides, oxygen, water or ammonia.

If the reaction heat is distributed, the local overheating can be avoided and the ammonia desorption from the solid phase is slower, thus NH_3 can be oxidized in the solid phase. After the total decomposition of permanganate ion (oxygen evolution is ended) the oxidation process also seems to be finished, and only ammonia and water can be observed (110–140°C) as decomposition products. It means that the active oxidants are the permanganate ion or its decomposition intermediates.

3.2. On the mechanism of thermal decomposition of NH_4MnO_4

Although the ignition characteristics of ammonia gas with oxygen gas and the flame nature under the thermal decomposition of NH_4MnO_4 are similar [3,10], the oxidation of ammonia in gas phase with

Table 1
Assignement and intensity maxima of the mass spectroscopic ions during the thermal decomposition of NH_4MnO_4 (covered with alumina)

m/z	Assignments[a]	Temperature ranges of single and double peaks (°C)		Max. intensities[b] of single and double peaks (arbitrary units)	
16	NH_2^+, O^+	70–160		5.9	
17	NH_3, OH^+	80–180		7.3	
18	H_2O	70–130	130–170	114	54
28	CO, N_2	70–130	130–180	13	20
30	NO^+	145–180		1.7	
32	O_2	70–115		7.5	
44	N_2O, CO_2	70–130	130–180	9.1	10.1

[a] The compounds refer to the probable source of the ions. The '+' charge sign indicates that the corresponding formula represents a mass spectrometric fragment ion.

[b] The intensities are normalized by the initial sample mass.

gaseous oxygen under thermal decomposition of NH_4MnO_4 is not probable, since no typical oxidation products of ammonia (N_2, NO, NO_2, N_2O) were found. The role of manganese oxides in the low temperature (around 100°C) oxidation of gaseous ammonia is also not probable [11].

At higher temperatures (130–190°C) another oxidation process occurs, where H_2O, N_2O NO, N_2 and a small amount of O_2 are formed as the main oxidation products. Above 145°C NO and H_2O are formed in the oxidation step and are retained. Since the decomposition reactions were carried out under argon atmosphere, this phenomenon should exclusively be the result of the reaction between ammonia and manganese oxides originated from permanganate anion.

The formation of N_2O in the thermal decomposition of ammonium salts of oxoanions chromate [12,13], dichromate [14], chlorate [15], perchlorate [14–20] or MO_4^{n-} metallates (MV, Mo and W) [21] is known. NH_4NO_3 is the possible precursor of N_2O and water as well according to the following equation:

$$NH_4NO_x + \Delta = N_2O_{x-2} + 2H_2O \qquad (2)$$

NO and N_2O always form together in the oxidation process of ammonia [11,19,20]. The presence of metal oxides, however, as potential catalysts [11,22] accelerate the decomposition of NH_4NO_3 resulting in the exclusive formation of N_2O. The experimental results led us to assume that during the first decomposition step of NH_4MnO_4 as a temporary compound, NH_4NO_3 can be formed.

There is another possibility for the formation of oxidation products N_2, NO or N_2O in the second decomposition step, too. It is the oxidation of adsorbed ammonia by manganese oxides. On the basis of some references [15,23] N_2O can also be formed in the oxidation of ammonia. In this oxidation processes, e.g. by oxygen, nitrogen and nitrogen oxides (NO or also N_2O) are produced. The amount of N_2O formed is temperature-dependent [23] and so is the increase in the presence of various catalysts [15] which inhibit the further decomposition of the previously formed N_2O. Since the catalytic effect of manganese oxides (MnO_2 and Mn_2O_3) which are formed in the thermal decomposition of ammonium permanganate (the composition of oxide phase is temperature dependent [6]) in the ammonia oxidation process at relatively low temperatures [11] is well defined, in the second oxidation step the manganese oxides play an important role in the formation of nitrogen oxides.

At higher temperatures there is a very little ammonia in the solid phase, thus the oxidation process is not significant.

Not only does the presence of gaseous products (NH_3, H_2O or $O_{2,}$), but the presence of dislocations (due to formation of thermal decomposition products) which cause stresses in crystal lattice also plays an important role [4] in the thermal decomposition process of NH_4MnO_4.

It is known [3] that ammonium permanganate decomposes slowly at room temperature. However, the longer storage of this salt at the same temperature decreases the decomposition rate compared with unstoraged salt [4]. With increasing number of dislocations (formed under storage) the number of active stress centers in crystal lattice is increased. Under fairly long storage, the crystal lattice is interrupted due to the high rate of decomposition, therefore, the role of stresses ceases.

In the slow decomposition of NH_4MnO_4 at room temperature the hydrogen bonds which are present between the hydrogen of ammonia and the oxygen of permanganate also [24] play an important role. These interactions are the active centers of redox processes between permanganate ion and ammonia (via formation of Mn-oxides) resulting in crystal defects and dislocations.

The presence or absence of NH_4NO_3 or NH_4NO_2 as precursors of N_2O or N_2 is also important in thermal decomposition of NH_4MnO_4. Some authors have detected ammonium nitrate among the solid decomposition products of ammonium permanganate (under vacuum in oil as heat conducting media [2] or under atmospheric condition [6]). However, in the residue of the totally decomposed NH_4MnO_4 in vacuum neither ammonium nor nitrate ions were found [3] at 100°C. Under these conditions (vacuum, in the absence of retarding media e.g. oil) the ammonia is desorbed from manganese oxides, and further oxidation yielding ammonium nitrate can be excluded. The formation of ammonium nitrite together with ammonium nitrate is also detected [9] in the reaction of NH_4MnO_4 and NH_3, but NH_4NO_2 decomposes above 70°C due to its thermal instability. The formation of N_2 starts at 70°C, see Table 1 or Fig. 1, thus the origin of N_2 between 70–130°C from decomposition reaction of NH_4NO_2 cannot be excluded. Desorption of ammonia does not occur under atmospheric pressure (sorptioned ammonia have been detected in solid phase decomposition products of NH_4MnO_4 above 100°C [6]), thus the oxidation of ammonia to ammonium nitrate may take place. In the presence of ammonium nitrate the decomposition of NH_4MnO_4 is slower [3] than in the case of pure salt, due to the endothermic effect of the phase transitions of ammonium nitrate [13] at the temperature where NH_4MnO_4 decomposes.

The mechanism of catalytic action is based on the presence of superoxide ion (O_2^-) on the surface of manganese oxides [11]. Increasing the partial pressure of oxygen the formation of (O_2^-) covered sites on manganese oxides are increased, but the presence of oxygen can accelerate the oxidation thermal decomposition [3] process of ammonium permanganate.

Furthermore, by raising the temperature the ammonia acts as a reducing agent towards MnO_2 by the formation of Mn_2O_3.

4. Conclusions

In the thermal decomposition of ammonium permanganate the main reaction is a simple permanganate decomposition process by the formation of oxygen and manganese oxides, as well as water and ammonia. The gas phase oxidation of ammonia by oxygen is not detectable.

The possible intermediates of low-temperature decomposition reaction of NH_4MnO_4 are ammonium nitrite or nitrate, then these primer decomposition intermediates further decompose to N_2, N_2O, or H_2O. Some part of ammonia sorptioned on hydrated Mn-oxides originates from permanganate ion. At increasing temperature the evolution of ammonia and water (retarded in solid manganese oxide phase) starts at about 130°C and a new oxidation reaction takes place, where N_2O, N_2, NO and H_2O are released as oxidation products. The oxidation of adsorbed ammonia by manganese oxides via the superoxide active centers on the surface of manganese oxides is more feasible in the second oxidation step. The accelerating effect of oxygen in the thermal decomposition (including the redox reaction) of ammonium permanganate confirms the above meaning, because by increasing partial pressure of oxygen the covering of the surface of manganese oxides by O_2 molecules (precursors for (O_2^-) ions) increases as well.

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