Asian Journal of Chemistry Vol. 15, Nos. 3 & 4 (2003), 1859–1860

NOTE

Kinetic Study of the Thermal Decomposition of Barium Nitrate

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Kinetic studies on the thermal decomposition of barium nitrate with metal oxide catalysts, doped ionic impurities and after γ-irradiation have been carried out by dynamic thermogravimetry. The metal oxides have influence on the kinetics of the thermal decomposition. The effect of doped impurities and γ-irradiation did not show any profound influence on the decomposition.

Key Words: Thermal decomposition, Barium nitrate, Effect of metal oxides, Thermogravimetry.

Thermogravimetric studies of inorganic substances have been a subject of great interest in assessing the thermal stability of materials, their thermal fragmentation pattern under the influence of metal oxide catalysts, irradiation, etc. These studies paved the way for kinetic analysis of the situations and correlating with the topochemical aspects. As the pyrolytic methods could be used for synthetic purposes, catalytic effects of metal oxides have assumed much significance. Apart from the catalytic aspects, the metal oxides often react with the inorganic salts to give rise to technologically important mixed metal oxides also. The work reported is mainly on the influence of metal oxides on the pyrolysis of barium nitrate.

Dried and sieved AnalaR (BDH) sample of barium nitrate was used for the pyrolytic study. The metal oxides used were commercially available. The experiments were carried out in dynamic nitrogen atmosphere using a Perkin-Elmer Thermal Analyzer Model TGS-2. The TG data were analyzed using standard methods.

Barium nitrate on heating melted before decomposition and a typical single-stage TG curve was obtained. The kinetic analysis was done by the Coats-Redfern method[1]. The final product of thermolysis of most of the nitrates are the corresponding metal oxides[2]. The effects of metal oxides on the thermal decomposition of $NaNO_3$ using TiO_2, Al_2O_3, SiO_2, ZrO_2, etc. were studied[3]. The results were interpreted on the basis of the relative acidity of the oxides. Rudloff and Freeman[4] made a systematic study of the effect of metal oxides on thermal decomposition of chlorates and perchlorates. Nair *et al.*[5] studied the thermal

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behaviour of bromates under the influence of metal oxides and determined the kinetic parameters of the decomposition.

The effects of metal oxides on the thermal decomposition of barium nitrate are presented in Table-1. Among them the reaction involving $Ba(NO_3)_2$ and TiO_2 is quite interesting as it provides a method for the synthesis of $BaTiO_3$. Equimolar mixture of reactants when heated at 1170 K produced $BaTiO_3$ in quantitative yield[6]. $BaTiO_3$ is a ferro-electric material and it has great technological importance.

The size of $Ba(NO_3)_2$ particles had some effect on the decomposition energetics. When the particle size was changed from 45 to 125 microns, the E_a values changed from 140 kJ to 193 kJ and the entropy of activation changed from -148 J K^{-1} to -90 J K^{-1}. The doped cation impurities like Na^+ and K^+ or anion impurities like Cl^-, Br^- did not have much influence on the energetics of the pyrolytic decomposition of the salt. This is due to the melting of the salt near the procedural decomposition temperature. Irradiation of the salt with γ-rays lowered E_a and ΔS values. The T_i and T_s values were also lowered in proportion to irradiation dosage.

TABLE-1
EFFECT OF METAL OXIDES ON $Ba(NO_3)_2$ SAMPLE

Kinetic parameter determined by the Coats-Redfern method

S.No.	Metal oxide	E (kJ mol^{-1})	Z (s^{-1})	ΔS (J K^{-1} mol^{-1})
1	—	144.3	1.2×10^5	–157.0
2	Al_2O_3	184.4	1.4×10^7	–118.1
3	TiO_2	312.1	3.2×10^5	42.6
4	Cr_2O_3	228.1	5.0×10^{11}	–29.6
5	MnO_2	160.6	2.9×10^6	–130.7
6	Fe_2O_3	182.4	1.2×10^8	–98.7
7	CuO	138.2	6.1×10^4	–162.8
8	ZnO	136.5	2.5×10^4	–170.7
9	ZrO_2	165.7	2.5×10^6	–132.25
10	La_2O_3	127.2	8.0×10^3	–180.1
11	ThO_2	165.9	7.4×10^5	–142.4

$Ba(NO_3)_2$ and metal oxide in the ratio 4 : 1 by mass.
Partial size 53–63 microns. Heating rate: 20° min^{-1}

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(*Received: 17 February 2003;* *Accepted:* 12 May 2003) AJC-3126