

م.د. ابتسام جميل داود

قسم الكيمياء - كلية التربية - ابن الهيثم - جامعة بغداد

الخلاصة

تضمن البحث دراسة تفاعلات الحالة الصلبة بين اوكسيدي الباريوم الثنائي والفناديوم الخماسي باستخدام جهاز التحليل الحراري ((الدريفتوغراف ((0 ومن ثم التعرف على التصرف الحراري التحليلي لنواتج تلك التفاعلات . وقد أيدت فحوص الأشعة السينية الحيودية التي أجريت على تفاعلات الصلب - صلب للاو كسيدين إلى تكون المركبات :



هذا وتم تحديد مراحل الاستقرار الحراري ودرجات حرارة الانصهار ومعادلات التفاعلات . كما أجريت دراسة تتعلق بالتحلل الحراري وحيود الأشعة السينية لأكسيد الباريوم النقي 0

**THERMOCHEMICAL STUDY OF SOLID
STATE REACTIONS BETWEEN BaO AND
 V_2O_5**

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Asst.Instructor.IBTISAM JAMEEL

*- Department of chemistry ,College of Education, Ibn-Al
)Haitham University of Baghdad , Adhemiya Baghdad , (Iraq*

ABSTRACT

The solid state non isothermal synthesis of mixed oxides of barium and vanadium and their subsequent thermoanalytical behaviour at high temperatures have been performed with derivatograph . Solid - Solid interactions between BaO and V₂O₅ occurred resulting in the formation of V₃O₇ , BaVO₃ , V₃O₅ , and Ba₅V₅O₁₅ . their identities have been confirmed by X- ray diffractometry and their thermal stabilities, melting temperatures , and stoichiometric formation equations have been established. In all synthesis and decomposition reactions oxygen was liberated .The X- ray diffraction and thermal analysis of pure commercial BaO have also been carried out .

INTRODUCTION

V₂O₅ is important for the catalytic oxidation of SO₂ to SO₃ [1]. Mixed oxides of vanadium with other metals such as Mo and Ti have been used extensively catalysts in organic synthesis and mainly in polymerisation of C₂H₄ to polyethelyne [2-4]. Thethermochemical behaviour of systems as V₂O₅ –PdO , and V₂O₅ – MgO , V₂O₅ –BaClO₄ .3H₂O have been investigated in preceding papers [4-8] . Because of the fact that V₂O₅ is predominantly acidic , it is expected to react with the more basic BaO to yield metal vanadates or vanadites , but so far as we are aware the direct solid state synthesis has not been performed . In this paper we report on the solid 1- solid 2 interactions between BaO and V₂O₅ and their intermediate and final products .

EXPERIMENTAL

:Materials

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BaO(purum , Fluka AG Buchs) , V_2O_5 and $\alpha\text{-Al}_2O_3$ of analytical purity (BDH) were used without further purification

Apparatus and procedure:

The thermoanalytical measurements were performed by means of the MOM photorecording derivatograph .

The procedure followed in the preparation and identification of reaction . intermediates and final thermal analysis products was that described previously [9-10] . pure (MOM) quartz was used to check the performance of the DTA part of the instrument.

Instrumental settings:

Sample size :200 mg

Sample and reference holders; Platinum cylindrical crucible

MOM medium size.

Reference material : $\alpha\text{-Al}_2O_3$ excicated at 1300°C .

Atmosphere :Ambient static air.

Heating rate : 10°C min .

Heating program :Ambient to 1050°C .

Recording sensitivities:

Thermogravimetry (TG)	200 mg
Derivative thermogravimetry (DTG)	1/10
Defferential thermal analysis (DTA)	1/10

RESULT AND DISCUSSION

Derivatographic behaviour of BaO

The derivatographic behaviour of pure V_2O_5 has been discussed previously [5] . X-ray diffractometry [11] has proved that commercial BaO contains traces of impurities such as BaO_2 [12] .

Fig –1 shows the TG and DTA thermal profiles of BaO , from which it is seen that the sample gradually lost weight beyond 70°C (2mg) due to decomposition of BaO_2

into BaO and O₂. Thereafter, it gained weight (350-370°C) by partial oxidation of BaO into BaO₂ (gain of 1%). The DTA curve indicates that an endothermic phase change occurred at T_{max} 240°C which could be used as qualitative thermal evidence for the presence of BaO. The typical melting endotherm of BaO appeared at T_{max} 380°C. On cooling the BaO melt a snow-white solid BaO product was obtained. Between 380-470°C no appreciable mass loss was observed on the TG curve. Afterward, the curve gradually descended due to slow evolution of oxygen up to 1050°C because of the decomposition of BaO with increasing temperature. This behaviour is identical to other others findings [13-14].

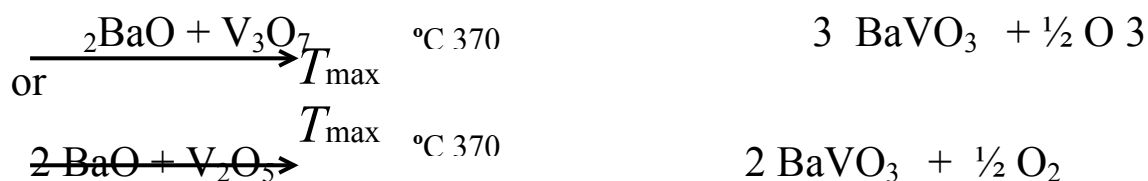
Derivatographic behaviour of the BaO-V₂O₅ system

Fig.1 shows the TG curves for molar ratios : 1:6, 1:3, 2:3, 1:1, and 2:1 BaO: V₂O₅ which have mass losses over the range 80-120°C of 1.5, 2, 2.2, 2.5 and 2mg respectively ; with matching endothermic peaks (T_{max} 110°C) on the respective DTA curves. The peak was absent in the DTA curves of both pure BaO or V₂O₅, which implies that a reaction between BaO and V₂O₅ accompanied by a loss of oxygen has occurred between about 90 and 120°C.

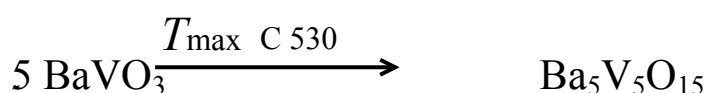
Subsequently two samples of 1:1 molar mixture were heated up to 200 and 280 °C respectively cooled and analysed by X-ray diffraction. The appeared strong lines : 3.674 2.595 2.135 2.013 Å belongs to V₃O₇ [15]. It is worth noting that the areas of these decomposition endotherms depended on the quantities of both V₂O₅ and BaO (mass effect) of each ratio. As the ratio approached stoichiometric, the d-

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lines for both BaO and V_2O_5 disappeared and the endothermic peak corresponding to the formation of V_3O_7 becomes larger. An unstable intermediate, perhaps a mixed oxide adsorption complex, has been formed on grinding the BaO- V_2O_5 molar ratio mixtures below 90°C for a relatively long period. The identity of this complex could not be confirmed by X-ray diffraction for unknown reasons. The small endotherm appearing at 240°C due to the crystalline phase change of unreacted BaO, and indicates its presence. The DTA curves had sharp exotherms accompanied by abrupt mass loss, with a common T_{max} at 370°C , indicating exothermic solid-solid reactions between the two oxides. The areas of these exothermic peaks (the enthalpies) were proportional to the amount of BaO in the ratio, and since the relative area of the 2:1 ratio was the greatest among all mole ratios, it is likely that two BaO molecules reacted with one molecule of V_2O_5 to give half a mole of oxygen plus heat evolution. This is supported by the fact that the XRD patterns for samples of this molar ratio heated to 450°C were devoid of BaO d-lines, and those of V_2O_5 were diminished while d-line belonging to a new compound formed (3.129, 3.015, 2.079, 1.960, 1.699 and 2.172 Å). The most intense of these lines matched those of $BaVO_3$ [16]. This clearly shows that that the stoichiometric reactions could be written as



The large sharp endotherm at T_{max} 530°C pretained to the melting of $BaVO_3$. Both TG and DTA curves indicate the partial decomposition of $BaVO_3$ aided the melting process in all molar ratio with a minimum for 2:1 where a relatively small exotherm appears at T_{max} 530°C. The XRD patterns for samples of this ratio cooled from 600°C showed the absence of V_2O_5 , BaO and $BaVO_3$ d-line and the appearance of strong lines belonging to $Ba_5V_5O_{15}$ or $(BaVO_3)_5$ (3.199, 2.873, 2.149 and 2.91 Å) [17]; suggesting the following equation for the over-all polymerization reaction.



The polycrystalline mixed oxide then very slowly degrades through two consecutive stages shown on the DTA curves by two endotherms with T_{max} at 690 and 740°C respectively. X-ray diffraction of the decomposition products obtained after the first endotherm around 700°C indicated the presence of V_3O_5 (strong lines at 3.297, 2.86 and 2.640 Å) [18] of BaO and weak lines of V_2O_5 while the

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d-line of $\text{Ba}_5\text{V}_5\text{O}_{15}$ completely vanished . Thus the decomposition can be described by the following:



The endothermic peak at $T_{\max} 740^\circ\text{C}$ belonged to a phase change of one of the degradation products V_3O_5

The excess oxygen present in the synthesized compounds: V_3O_7 , BaVO_3 , $\text{Ba}_5\text{V}_5\text{O}_{15}$ and V_3O_5 , indicated their potentialities as oxidants and semiconducting catalysts

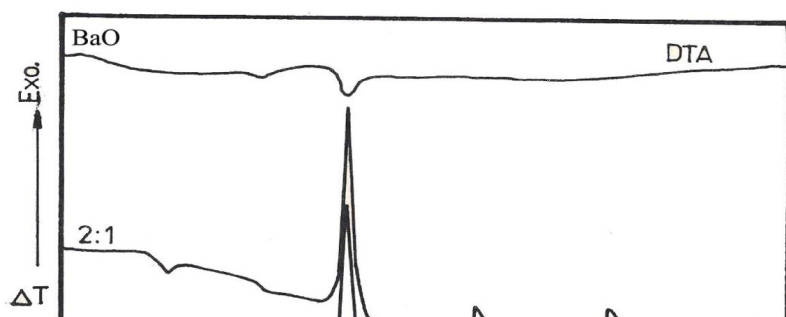
Microscopic and visual examination showed all prepared compounds to be different shades of orange ,except V_3O_5 which was dark gray. The thermal behaviour of molar ratio $\text{BaO}:\text{V}_2\text{O}_5$, also showed a large melting endotherm of 1:6 V_2O_5 at 645°C inferring that only a little V_2O_5 reacted with all BaO present. It is worth explaining that the unusual deviation from the DTA base-line of this ratio was due to variation of the heat capacity of V_2O_5 with rise of temperature [19] as well as those of the reaction products

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