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THE REACTION OF THE SPINEL FeV_2O_4 WITH Na_2CO_3 IN AN INERT ATMOSPHERE

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ABSTRACT

The thermal reactions of FeV_2O_4 with Na_2CO_3 in an inert atmosphere were studied using thermogravimetry, differential thermal analysis, evolved gas analysis and X-ray powder diffraction. The main products were found to be Fe, $Na_4V_2O_7$ and Na_3VO_4. In the presence of excess Na_2CO_3, Na_3VO_4 seems to be the main vanadium-containing product.

INTRODUCTION

The vanadium contents of titaniferous magnetite ore are almost without exception expressed as $\%V_2O_5$, which is the most stable vanadium oxide. The vanadium contents of the ore are, however, present as the mineral (coulsonite) which has a spinel structure with V^{III} replacing some of the Fe^{III} in the magnetite structure. A roast–leach industrial process is well known and is employed in the production of V_2O_5 and NH_4VO_3 from titaniferous magnetite ore [1]. According to Gabra and Malinsky, this involves the oxidation of the metals present in the ore, V^{III}, Fe^{III}, Cr^{III} etc., to the corresponding oxides which then react with the Na_2CO_3 according to the reaction [2]

$$M_xO_y + zNa_2CO_3 \rightarrow zNa_2O \cdot M_xO_y + zCO_2$$

The optimisation of the controlling parameters of this process is a well developed art rather than a science. The conditions are not founded on a thorough understanding of the fundamental chemistry involved in the reaction of FeV_2O_4 with the sodium salt, Na_2CO_3 or Na_2SO_4. This lack of

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information concerning the mechanism of the oxidation of FeV_2O_4, and the reaction of the spinel and its oxidation products with Na_2CO_3, initiated this project.

The reaction of FeV_2O_4 with Na_2CO_3 in an inert atmosphere was studied in order to investigate the validity of the belief that O_2 is essential for the formation of water-soluble vanadates, i.e. Na_2CO_3 cannot contribute to the oxidation of FeV_2O_4. The results of the investigation are discussed in this paper.

EXPERIMENTAL

Sample preparation

FeV_2O_4

The method used for the preparation of FeV_2O_4 was a slightly modified version of one described by Goodenough and co-workers [3]. The method consists of the following steps.

(i) A 2 : 1 molar ratio mixture of V_2O_3 and Fe_2O_3 was stirred in petroleum ether for 18 h. This produced a homogeneous mixture which substantially reduced the time needed for complete conversion to FeV_2O_4.

(ii) The mixture was then placed in a resistively heated tube furnace at 1100 °C under a 4.5 : 1 ratio $CO:CO_2$ dynamic atmosphere. The temperature as well as the atmospheric conditions were maintained for at least 24 h.

(iii) The FeV_2O_4 was then cooled to ambient temperature in the CO/CO_2 atmosphere and analysed for Fe_2O_3 and V_2O_3 by X-ray powder diffraction.

(iv) Steps (ii) and (iii) were repeated until no starting materials were detectable. The total time needed for complete reaction was 48 h (c.f. 72 h if the method of Goodenough was followed).

FeV_2O_4/Na_2CO_3 mixtures

Three mixtures with $FeV_2O_4:Na_2CO_3$ mole ratios of 1 : 1, 2 : 5 and 1 : 5 were prepared. Anhydrous Na_2CO_3 (Merck analytical grade) was ground to a fine powder and air-dried at 200 °C for 24 h. Accurately weighed FeV_2O_4 and Na_2CO_3 were mixed by stirring the powders in petroleum ether for 20 h. The mixtures were then vacuum dried and thereafter air-dried at 100 °C. The mixtures were stored in a desiccator over silica.

Thermal analysis

Thermogravimetric (TG) experiments were carried out on a Du Pont 990 thermal analyser with a 951 thermogravimetric analyser unit. A heating rate of 2 K min^{-1} was used in all experiments. Differential scanning calorimetry data were collected using a Perkin–Elmer DTA 1700 differential thermal analyser operated in the DSC mode. Platinum sample and reference cups were used. All thermal experiments were recorded in a dynamic atmosphere of pure Ar with a flow rate of 100 cm^3 min^{-1}. In order to remove any trapped air from the instruments and to thus reduce the possibility of O_2 oxidation of the spinel, the instruments were successively flushed with Ar for 20 min, evacuated and flushed again with Ar for 1 h prior to the start of each experiment.

Evolved gas analysis (EGA)

Qualitative EGA studies were conducted by passing the outlet gases of the TG through a Shimadzu GC-4B gas chromatograph with a flame ionization detector (FID). This GC was modified during a previous study to separate and detect both CO and CO_2 [4]. A Carbosieve II (80–100 mesh) column was used to separate the evolved CO and CO_2. After separation the gas was passed through a small reactor containing Fischer–Tropsch (FT) catalyst which was kept at a constant temperature of 400 °C. This FT catalyst converts both CO and CO_2 to predominantly methane in the presence of H_2 (the carrier gas in the GC) which is detectable by an FID.

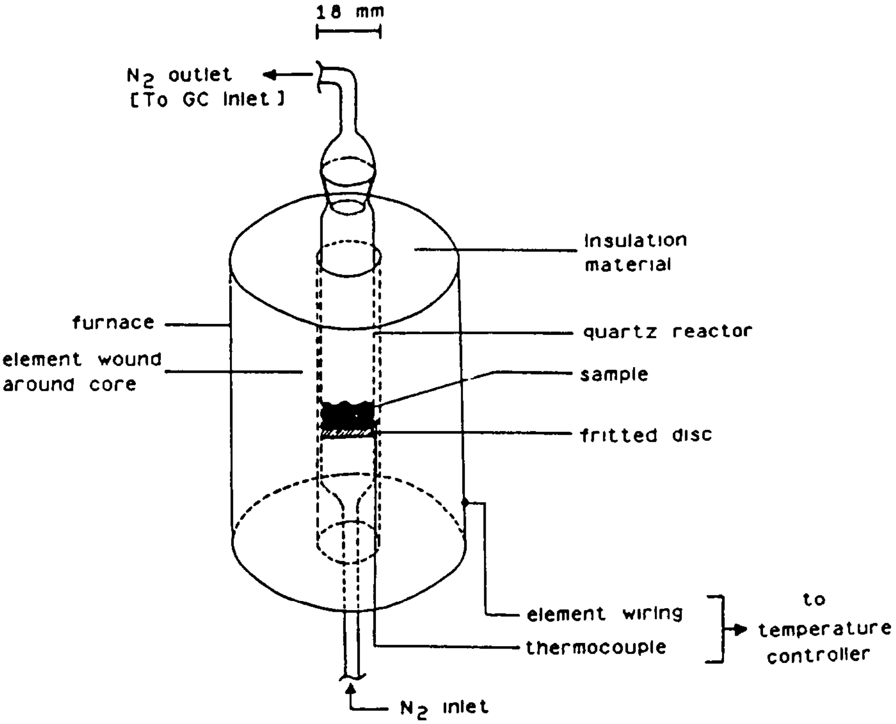

Fig. 1. Schematic representation of the reactor used in the EGA studies.

Quantitative EGA studies were conducted by replacing the TG with a reactor which is illustrated in Fig. 1. This was necessary because larger sample masses were required to obtain accurate results. Pure methane was used for calibration purposes.

X-ray powder diffraction (XRPD)

A Seifert MZ-IV diffractometer with Cu *Kα* radiation was used to record all powder patterns.

RESULTS AND DISCUSSION

The TG curves for the various mixtures are shown in Fig. 2. Evolved gas analysis, see Fig. 3, showed that both CO and CO_2 were evolved. The DSC curves, Fig. 4, suggest that various overlapping endothermic reactions are taking place.

The 1 : 1 mixture

A total mass loss of 11.1% at 730 °C was observed for this mixture. Quantitative EGA measurements showed that the evolved gas consisted of 53% CO_2 and 47% CO. X-ray powder diffraction, see Table 1, of the product showed that a large amount of unreacted spinel was present. Fe_3O_4, Na_3VO_4 and $Na_4V_2O_7$ were the major products. Traces of α-Fe and FeO were also detected.

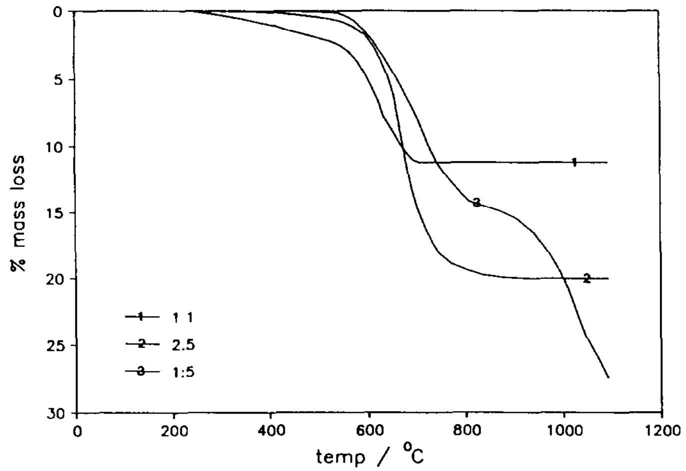

Fig. 2. TG curves for the three stoichiometric mixtures of FeV_2O_4/Na_2CO_3 in argon at a heating rate of 2 K min^{-1}.

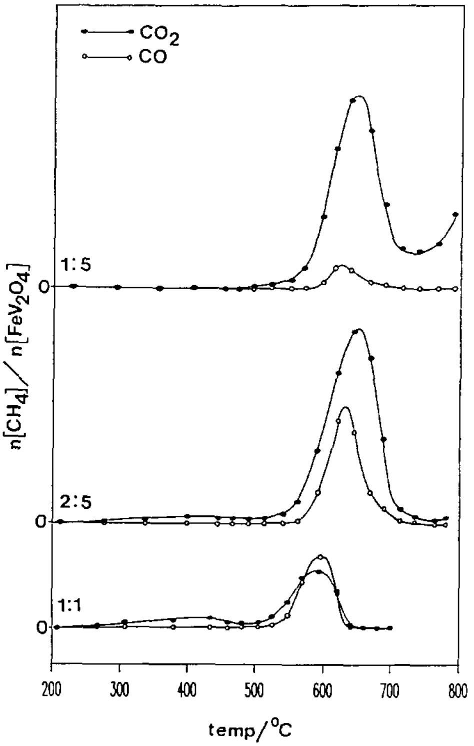

Fig. 3. Quantitative EGA curves expressed as the mole ratio of CH_4 detected to spinel present in the mixture.

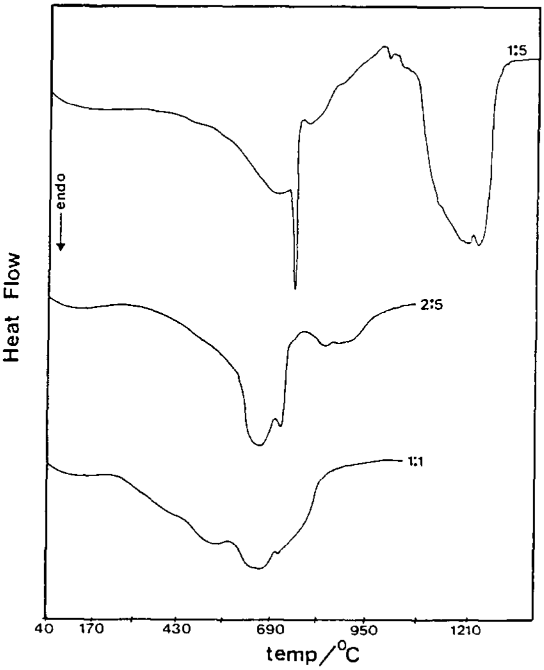

Fig. 4. DSC curves for the three stoichiometric mixtures of FeV_2O_4/Na_2CO_3 in argon.

TABLE 1

X-ray powder diffraction lines observed after the completion of the reaction of 1 mol FeV_2O_4 with 1 mol Na_2CO_3

d (Å)	Relative intensity	Substance	d (Å)	Relative intensity	Substance
6.33	10	Na_3VO_4	2.59	15	Na_3VO_4, $Na_4V_2O_7$
5.88	10	Na_3VO_4	2.55	100	FeV_2O_4
5.68	25	$Na_4V_2O_7$	2.53	40	Fe_3O_4
4.86	20	FeV_2O_4, Fe_3O_4	2.48	15	FeO, Na_3VO_4
4.40	15	Na_3VO_4	2.42	20	Fe_3O_4
4.34	25	Na_3VO_4	2.20	10	Na_3VO_4
4.28	15	$Na_4V_2O_7$	2.15	20	FeO, Na_3VO_4 $Na_4V_2O_7$
4.18	10	Na_3VO_4			
3.30	15	Na_3VO_4, $Na_4V_2O_7$	2.11	30	FeV_2O_4
3.23	15	$Na_4V_2O_7$	2.09	20	Fe_3O_4
2.98	45	FeV_2O_4, Fe_3O_4	2.03	15	α-Fe
2.86	30	$Na_4V_2O_7$	1.72	20	FeV_2O_4
2.84	30	Na_3VO_4	1.63	40	FeV_2O_4
2.79	20	Na_3VO_4, $Na_4V_2O_7$	1.62	25	Fe_3O_4
2.69	20	Na_3VO_4, $Na_4V_2O_7$	1.52	10	Na_3VO_4, $Na_4V_2O_7$
2.67	15	Na_3VO_4, $Na_4V_2O_7$	1.49	40	FeV_2O_4
2.65	15	Na_3VO_4, $Na_4V_2O_7$	1.48	30	Fe_3O_4

The 2 : 5 mixture

A mass loss of 20.0% was recorded for the mixture. The reaction was completed at 930 °C. The CO_2 content was 68% while the CO content was 32%. X-ray diffraction, Table 2, showed that the products were Na_3VO_4, $Na_4V_2O_7$ and α-Fe. No unreacted spinel or Na_2CO_3 were detected.

TABLE 2

X-ray powder diffraction lines observed after the completion of the reaction of 2 mol FeV_2O_4 with 5 mol Na_2CO_3

d (Å)	Relative intensity	Substance	d (Å)	Relative intensity	Substance
6.90	15	Na_3VO_4, $Na_4V_2O_7$	2.32	20	Na_3VO_4
4.49	35	Na_3VO_4	2.22	20	Na_3VO_4
4.44	40	Na_3VO_4	2.08	25	Na_3VO_4
4.38	50	Na_3VO_4	2.06	25	Na_3VO_4
3.84	20	Na_3VO_4	2.03	100	α-Fe, $Na_4V_2O_7$
2.92	30	$Na_4V_2O_7$	1.91	30	Na_3VO_4
2.84	50	Na_3VO_4, $Na_4V_2O_7$	1.76	20	Na_3VO_4
2.72	70	Na_3VO_4, $Na_4V_2O_7$	1.57	30	Na_3VO_4
2.69	50	Na_3VO_4	1.56	25	Na_3VO_4
2.61	20	Na_3VO_4, $Na_4V_2O_7$	1.43	20	α-Fe
2.56	15	Na_3VO_4			

The 1 : 5 mixture

The TG curve showed a reaction which was completed at approximately 800 °C and a second reaction up to 1000 °C, which is the maximum temperature of the TG furnace. This second reaction, with a peak at 1210 °C on the DSC curve, was ascribed to the decomposition of the excess Na_2CO_3. Product analysis at 800 °C indicated 92% CO_2 and 8% CO in the gas phase, while the solids were identified as Na_3VO_4, $Na_4V_2O_7$, α-Fe and unreacted Na_2CO_3. (The X-ray powder diffraction pattern was similar to that given in Table 2, except that Na_2CO_3 lines were detected.)

The DSC curves for the three stoichiometric mixtures are essentially similar between 200 and 1000 °C. A shift towards higher temperatures for completion of the reactions with increasing Na_2CO_3 content was observed. A similar observation has been made for the interaction of Cr_2O_3 with Na_2CO_3 [5]. This shift can be explained by the increasing availability of Na_2CO_3 for further reaction with $Na_4V_2O_7$ to form the most basic vanadate, Na_3VO_4, according to the reaction

$$Na_4V_2O_7 + Na_2CO_3 \rightarrow 2Na_3VO_4 + CO_2 \quad (1)$$

This would also explain the high $CO_2 : CO$ ratio observed as gaseous products during the reaction of the 1 : 5 mixture.

A single melting endotherm, which became more prominent with increasing Na_2CO_3 content, was observed at 714, 716 and 755 °C for the various mixtures. This melting endotherm is believed to be a complex eutectic melting of $Na_4V_2O_7$, Na_3VO_4 and Na_2CO_3. Eutectic melting of $Na_4V_2O_7$ and Na_3VO_4 has been reported by Kerby and Wilson and was found to vary between 615 and 850 °C depending on the concentrations: a 1 : 1 mixture melted at 750 °C [6].

From the results presented above, it is clear that similar reactions are taking place in the various mixtures. The same solid products, $Na_4V_2O_7$ and Na_3VO_4, were observed. The Na_2CO_3 content seems to determine the extent of the reactions. On this basis the following reaction scheme can be presented for the system

$$6FeV_2O_4 + 15Na_2CO_3 \rightarrow 3Na_4V_2O_7 + 6Na_3VO_4 + 3Fe_2O_3 + 15CO \quad (2)$$

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \quad (3)$$

$$2Fe_3O_4 + 8CO \rightarrow 6Fe + 8CO_2 \quad (4)$$

The total reaction would then be

$$6FeV_2O_4 + 15Na_2CO_3 \rightarrow 3Na_4V_2O_7 + 6Na_3VO_4 + 6Fe + 6CO + 9CO_2 \quad (5)$$

In the presence of excess sodium carbonate, the reaction continues according to reaction (1).

These results differ from those reported by Fotiev and Strelkov, who observed Fe_2O_3 as the only solid Fe-containing product and CO as the only gaseous product evolved [7]. It has been further demonstrated, therefore, that the formation of water-soluble vanadates from the spinel are possible in a sodium carbonate medium in the absence of oxygen.

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