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Note

NON-ISOTHERMAL DERIVATOGRAPHIC STUDY OF MoO_3–C AND Co_3O_4–C BINARY SYSTEMS

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ABSTRACT

High temperature reactions between graphite (C) powder and MoO_3 or Co_3O_4 were investigated in a static air atmosphere using a MOM derivatograph. Surprisingly, graphite completely prohibits the expected reduciton of MoO_3 and partially inhibits that of Co_3O_4. The former catalytically lowers the onset combustion temperature of graphite by about 90 °C and the latter by about 190 °C. Although both oxides significantly enhance the oxidation of graphite, Co_3O_4 leads to complete conversion of graphite into gaseous products of carbon and therefore is an ideal p-type semiconductive catalyst. X-ray diffraction and evolved gas analysis were employed to identify the intermediate and final products.

INTRODUCTION

Thermoanalysis of MoO_3 and Co_3O_4 has been described previously [1]. Electrolytic graphite is a porous material. Its porosity and therefore reactivity increases as the temperature rises. It is a powerful reducer for metallic oxides such as molybdenum, vanadium, boron, tantalum, aluminium and niobium oxides; with these refractory metals it forms carbides at high temperatures. Graphite intercalation compounds have been used as catalysts in industry [2]. Because of its high melting point (3500 °C), adsorptivity, electrical conductivity and thermal conductivity graphite has numerous useful scientific and industrial applications.

The aim of this study is to determine the relationship between the thermochemical activity of graphite (e.g. oxidation and reduction) and that of each of the catalysts MoO_3 and Co_3O_4; the activities cause some changes in the DTA and TG curves.

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EXPERIMENTAL

Reagents and samples

Co_3O_4, MoO_3 and graphite were puriss quality reagents obtained from Fluka AG Buchs (Switzerland). Dry, finely ground mixtures containing 25 wt.% or 50 wt.% Co_3O_4 with graphite and 25 wt.% or 75 wt.% MoO_3 with graphite were prepared.

Apparatus and analysis

Instrumental parameters are presented in Table 1. X-ray diffraction (XRD) patterns of the solid intermediate and final products were measured as described previously [3]. Evolved gas analysis was carried out as instructed in the instruction manual of the manufacturer [4].

RESULTS AND DISCUSSION

Derivatographic behaviour of graphite

The TG and DTA curves are presented in Fig. 1. Graphite remains thermally stable up to 580 °C. Thereafter slow degradation due to graphite oxidation (CO and CO_2 formation) begins and continues to the ceiling temperature of the heating programme where a weight loss of about 25 wt.% is observed within a single TG step. The DTA curve exhibits a small exothermic peak at $T_{max} = 350\,°C$ which can be attributed to a change in crystal structure of graphite. Another sharp endothermic peak is observed at $T_{max} = 490\,°C$ due to a polymorphic phase change (hexagonal to rhombic)

TABLE 1

Instrumental variables for the derivatographic analysis

Sample weight	200 mg
Reference material	α-Al_2O_3
Holders	Platinum, size 3
Heating rate	10 °C min^{-1}
Heating programme	Ambient–1050 °C
Grain size of samples	−100 mesh
Atmosphere	Static air
Sensitivities	
TG	200 mg
DTG	1/10
DTA	1/10

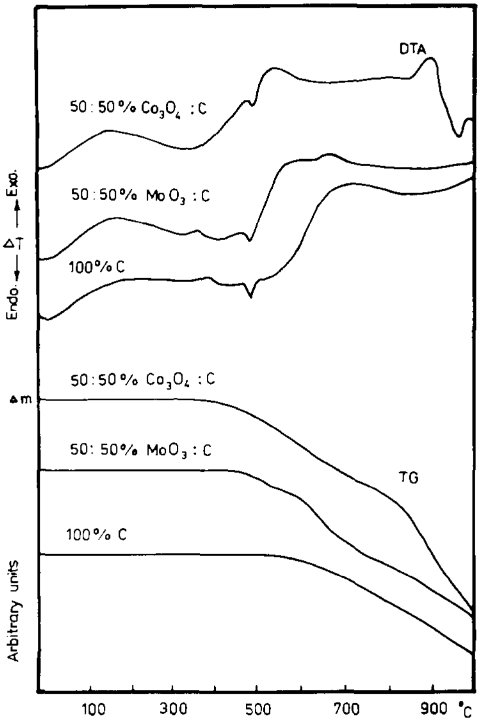

Fig. 1. TG and DTA curves of graphite and MoO_3–C and Co_3O_4–C mixtures.

[5]. The resemblance (Table 2) between standard and observed XRD patterns at 1000 °C indicates the reconversion of the rhombic to the hexagonal form.

Derivatographic behaviour of the MoO_3–C system

Mixtures containing 25 wt.% and 75 wt.% MoO_3 in graphite were subjected to the heating programme (Table 1). Careful scrutiny of the TG and DTA curves (Fig. 1) shows that no reaction occurs between MoO_3 and graphite throughout the complete heating programme. Surprisingly, graphite inhibits the melting and vaporization of MoO_3. This is demonstrated by

TABLE 2

Standard (ASTM) and observed XRD patterns of graphite samples sintered at 1000 °C

Standard	d (Å)	3.36	1.68	2.03
	I/I_0	100	80	50
Observed	d (Å)	3.36	1.68	2.03
	I/I_0	100	80	50

TABLE 3

Standard (ASTM) and observed XRD patterns of pure MoO_3 and of sample mixtures with graphite sintered at 1000 ° C [6]

Standard	d (Å)	3.26	3.81	3.46	6.96
	I/I_0	100	82	61	35
Observed	d (Å)	3.26	3.80	3.46	6.96
	I/I_0	40	70	100	90

measuring the XRD patterns for mixtures before (Table 3) and after heating (for samples sintered at 400 ° C and 1000 ° C). All XRD patterns are identical. Figure 1 shows that MoO_3 catalytically lowers the temperature of graphite combustion from 580 to 490 ° C. The combustion has a higher exothermicity at $T_{max} = 640\,^\circ C$ which can be attributed to a secondary oxidation process

$$CO + \tfrac{1}{2}O_2 \xrightarrow{\Delta} CO_2$$

The TG curve indicates that the combustion occurs in two distinct steps and a third overlapping one. Similar results are obtained for the 75 wt.% system except that the onset temperature is lowered to 470 ° C instead of 480 ° C. Thermoanalysis of the MoO_3–C system indicates that MoO_3 acts as a semiconductive catalyst (p-type), lowering the activation energy of the combustion process. In the presence of the catalyst the single combustion step of graphite is fragmented into three steps with the formation of CO and CO_2. The loss of weight is equivalent to 75 wt.% of graphite. In the absence of catalyst, only 50 wt.% of graphite is lost. The temperatures of these effects are dependent on the content of catalyst.

Derivatographic behaviour of the Co_3O_4–C system

The TG and DTA curves of the 50 wt.% graphite–Co_3O_4 system are shown in Fig. 1 (the 25 wt.% system is not shown for brevity). The onset temperature for pure graphite combustion is depressed by 190 ° C to 390 ° C. This is accompanied by a loss in weight due to both the combusiton of graphite and the partial decomposition of Co_3O_4 into CoO and O_2. XRD patterns of samples sintered at 1000 ° C indicate the presence of Co_3O_4 [7] and CoO [8] (see Tables 4 and 5 respectively). The identification of CoO and Co_3O_4 in the final products demonstrates the partial inhibition by graphite of the reduction of Co_3O_4. No graphite is detected in the final product due to its complete combustion. It seems that Co_3O_4 acts as a promoter for combustion. Only 25 wt.% of pure graphite is combusted in the absence of the oxide and the rest is detected in the final product.

TABLE 4

Standard (ASTM) and observed XRD patterns of pure Co_3O_4 and of a mixture with graphite sintered at 1000 °C

Standard	d (Å)	2.44	1.43	2.86
	I/I_0	100	50	40
Observed	d (Å)	2.44	1.43	2.86
	I/I_0	100	50	40

TABLE 5

Standard (ASTM) and observed XRD patterns of pure CoO and of a mixture of CoO with Co_3O_4 sintered at 1000 °C

Standard	d (Å)	2.13	2.46	1.51
	I/I_0	100	80	50
Observed	d (Å)	2.13	2.46	1.51
	I/I_0	100	80	50

The TG curve (Fig. 1) indicates that after 490 °C the combustion rate increases rapidly in the presence of Co_3O_4. Since the typical exothermic peak of graphite at $T_{max} = 350\,°C$ disappears, a redox reaction between graphite and Co_3O_4 must start at temperatures lower than 350 °C and this thermally neutralizes the peak by an endothermic process. In the presence of MoO_3 [1] this exothermic peak does not disappear, confirming the lack of reaction between this oxide and graphite.

CONCLUSIONS

The results obtained from the thermoanalysis of the two binary systems suggest the following conclusions.

(1) Graphite inhibits the thermal degradation of MoO_3, but the latter catalytically lowers the onset combustion temperature by about 90 °C. The exotherm at $T_{max} = 350\,°C$ does not disappear.

(2) The onset temperature of the combustion of graphite is lowered by 190 °C due to the catalytic effect of Co_3O_4. However, decomposition of about 7 wt.% Co_3O_4 occurs at the low temperature of 390 °C instead of at 955 °C in pure Co_3O_4 [3]. Co_3O_4 enhances the complete combustion of graphite in the samples.

(3) The extent of the combustion of graphite depends on the percentage of each oxide and reaches a maximum at 50 wt.%.

(4) Graphite intercalation compounds of molybdenum and cobalt are not detected perhaps because the heating programme temperatures are not high enough to bring about their formation.

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