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THERMAL ANALYSIS OF CHROMIUM(III) AND CHROMIUM(VI) SYSTEMS WITH SILICA AND SODIUM SILICATE

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Sodium silicate, or a mixture of silica and sodium carbonate, reacts with chromium(III) oxide in the presence of oxygen to give sodium chromate, within the approximate temperature range 300–900°. Above 900° the reaction is reversed and chromium(III) oxide regenerated.

It has been long known in the chrome chemical industry that an ore with a high silica content produces a low yield of chromium(VI). Yet it is also known that sodium silicate, a product of the reaction between sodium carbonate and silica, will produce a considerable degree of oxidation of chromium(III) when heated in air with chrome ore. This paper describes some experiments designed to clarify these apparently contradicting results.

Experimental

Thermoanalytical results were measured using a Stanton thermobalance fitted with a differential thermal analysis attachment. Anhydrous sodium silicate was prepared from the pentahydrate by heating to 600°. Precipitated amorphous silica was prepared and dried at 600°. Laboratory grade chromium(III) oxide, "AnalaR" sodium chromate and sodium carbonate were used. Chrome ore was supplied by Albright and Wilson Ltd.

Results

The DTA curve of sodium silicate exhibited only one feature – a reversible endotherm at 1082° due to fusion. A 1 : 1 mixture of chromium(III) oxide and silica gave no reaction up to 1100°. Sodium chromate showed two reversible endotherms – the first at 414° due to a polymorphic transition and the second at 785° resulting from fusion. Addition of sodium silicate (1 : 1) to sodium chromate did not affect these results. (The National Bureau of Standards Circular 500 quotes 413° and 792° for the two sodium chromate values.) The reaction of sodium carbonate and silica

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$$

began (from DTA results) at 300° and ended at 860°. Throughout its course it was weakly endothermic with a sharp fusion peak at 854°.

The DTA of a 1 : 2 chromium(III) oxide and sodium silicate sample showed a weak endotherm beginning at 550° and finishing at 850° with a fusion peak at 778°. TG showed a steady increase in weight over the same temperature range, corresponding to the reaction

$$Cr_2O_3 + 2Na_2SiO_3 + 1^1/_2\,O_2 \rightarrow 2Na_2CrO_4 + 2SiO_2$$

At 850°, the weight change corresponded to 35% oxidation – confirmed by subsequent analysis for chromium(VI). Above 1000° the sample lost weight slowly.

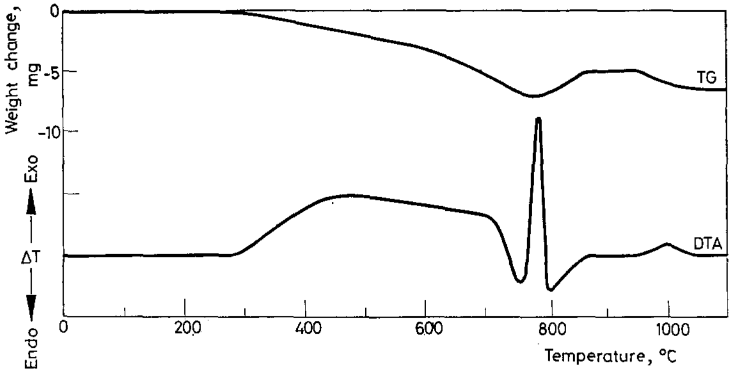

Fig. 1. Simultaneous DTA/TG of Cr_2O_3–Na_2CO_3–SiO_2 2 : 1 : 1 mixture

The DTA/TG of the system Cr_2O_3–Na_2CO_3–SiO_2 2 : 1 : 1 is given in Fig. 1. This shows that the sample began to lose weight (CO_2 evolution) at 280° when the DTA curve became endothermic. An endothermic region stretches from 280 to 730°. This was due to the evolution of CO_2 both in the reaction of sodium carbonate with silica and with chromium(III) oxide and the slow oxidation of the latter either by Na_2CO_3, or by Na_2SiO_3 and oxygen. The 730–860° region of the curve is taken up by an exotherm caused by the increasingly dominant oxidation reaction as carbon dioxide evolution ceased. This exotherm is split by a sharp reversible endotherm at 785° caused by the liquidus of the system (Na_2CrO_4 fusion). The sample weight continued to decrease between 730° and the liquidus temperature and then increased up to 800° when the oxidation reaction ended. On further heating the sample lost weight around 1000° with a corresponding weak endotherm appearing on the DTA curve. Both this weight change and thermal effect were reversible although on repeated cycling a slow decrease in the amount of chromium(VI) present was observed. This was repeated using a 1 : 1 : 1 instead of a 2 : 1 : 1 ratio and the results obtained were similar. Comparable runs were made but with no silica present, and stopping at a temperature of 850°. On analysis the samples with silica contained about 10% more chromium(VI).

Discussion

On comparing the Cr_2O_3–Na_2CO_3–SiO_2 and Cr_2O_3–Na_2CO_3 systems below 900°, the results show that the presence of silica has a beneficial effect as far as the oxidation of chromium(III) and chromium(IV) goes. This could arise in two ways. The first simply being that the additional solid phase in the system facilitates absorption of oxygen necessary for oxidation. The second factor arises from the fact that from about 300° on, two sodium salts are available for reacting with chromium(III) oxide, viz. sodium carbonate and sodium silicate. The decomposition of sodium carbonate, the reaction of sodium carbonate with silica, the reaction of sodium silicate with chromium(III) oxide are all endothermic with the only competing exothermic reaction being the oxidation of chromium(III) to chromium(VI). The net result of these reactions is the endotherm seen in Fig. 1 between 280 and 730°. From 730 to 860° the exothermic oxidation reaction dominates (apart from the liquidus endotherm) – after most of the carbon dioxide had been lost from the system.

However, between 900° and 1100°, silica causes the decomposition of 15–20% of the sodium chromate formed in the earlier reaction. Although in this case the reaction was almost completely reversible on cooling, it is not so in other instances more pertinent to the actual conditions of the industrial process. For example if a system $Na_2CrO_4 : SiO_2$: chrome ore, in the ratio 1 : 1 : 1 is taken, the reversibility of the reaction is only partial presumably because the sodium silicate produced in the back reaction can then further react with the iron and aluminium oxides as well as the chromium oxide in the ore. Also for the reaction to be completely reversible, oxygen must be readily accessible, and this is not necessarily the case at different stages in the industrial process.

The temperature at which sodium chromate starts to decompose in the presence of silica is lowered to below 900° in the presence of equal quantities of chrome ore.

Thus the effect of silica on the air oxidation of chromium(III) in the presence of sodium ion, is twofold. At lower temperatures, i.e. below 900°, it can prove beneficial. However, above 900° the reaction

$$Cr_2O_3 + 2Na_2SiO_3 + 1^1/_2\,O_2 \rightleftarrows 2Na_2CrO_4 + 2SiO_2$$

is reversed and the efficiency of the overall oxidation reaction lowered. The net result of the oxidation of chromium(III) oxide in the presence of silica will therefore depend on the temperature of the reaction and the availability of oxygen not only as the primary oxidation reaction takes place but also on cooling.

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Résumé — Le silicate de sodium ou un mélange de silice et de carbonate de sodium réagissent, en présence d'oxygène, avec l'oxyde de chrome trivalent pour former le chromate de sodium, approximativement entre 300 et 900°. Au-dessus de 900°, la réaction s'inverse et l'oxyde de chrome(III) est régénéré.

Zusammenfassung — Natriumsilikat oder eine Mischung von Siliziumdioxid mit Natriumkarbonat ergeben bei der Reaktion mit Chrom(III)oxid in Gegenwart von Luft im Temperaturbereich zwischen 300° und 900° Natriumchromat. Über 900° wird die Reaktion umgekehrt und Chrom(III)oxid zurückgebildet.

Резюме — Силикат натрия или смесь кремния и карбоната натрия реагирует с окисью хрома (III) в присутствии кислорода, давая хромат натрия в области температур 300—900°. Выше 900° эта реакция обратима и окись хрома регенирируется.