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THE EFFECT OF CATALYSTS DURING THE CARBOTHERMIC REDUCTION OF MANGANESE DIOXIDE

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ABSTRACT

Manganese dioxide is reduced by graphite first to Mn_2O_3, then to Mn_3O_4 and MnO, followed by Mn_5C_2, which then reacts with the remaining MnO to form metallic manganese. This reduction process is accelerated strongly by additions of K_2CO_3 or Na_2CO_3, and to a lesser extent by additions of CaO, Al_2O_3 and MgO. Silica retarded the reduction kinetics.

INTRODUCTION

Manganese ores often contain manganese dioxide which is reduced by solid carbon to ferromanganese in a submerged-arc furnace [1,2]. These ores contain gangue minerals in addition to manganese oxides and carbonates, which may have an effect on both the nature of the reduction products and the kinetics of reduction. However, very little is understood about the nature of these reduction processes. Grimsley et al. [2] observed that manganese ore rapidly reduced to MnO and $CaMn_2O_4$ which then react to form $(Fe,Mn)_7C_3$. King and Brown [3] modelled the movement of the topochemical interface during the reduction of manganese ores. Rankin and van Deventer [4] argued that the reduction of manganosite by graphite proceeds by way of carbon dioxide as a gaseous intermediate, while van Deventer [5] investigated the effect of gangue components on the reduction of manganosite.

It is the aim of this paper to explore the influence of catalysts, including gangue constituents, on the reduction of manganese dioxide by graphite.

EXPERIMENTAL

The experimental procedure was essentially the same as that described in earlier papers [4,5]. Mixtures of high purity MnO_2 (2.0 g), graphite (0.553 g) and SiO_2, MgO, Al_2O_3, CaO, Na_2CO_3 or K_2CO_3 (0.20 g) of particle size

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100% < 75 μm were reacted in purified argon at 1350 °C during thermogravimetric experiments. The solid reaction products were subjected to X-ray diffraction (XRD), and the product gas analysed for CO_2.

RESULTS AND DISCUSSION

It was found that the P_{CO}/P_{CO_2} ratio was between 17 and 20 for the first 5 min and then increased to about 115 for the rest of the run. If the evolved CO_2 is considered to be insignificant, then the fractional conversion X is defined as

$$X = \frac{\Delta m}{m} \cdot \frac{M_{MnO_2}}{2M_{CO}}$$

where Δm = registered mass loss; m = initial mass of sample; M_i = molecular mass of i.

Kinetic results are presented in Fig. 1. It is evident that K_2CO_3, Na_2CO_3, MgO, CaO and Al_2O_3 all accelerated the reduction of MnO_2 by graphite. This was probably caused by catalysis of the Boudouard reaction by these additives [5]. The effects of Na_2CO_3 and K_2CO_3 were more pronounced than those of CaO, Al_2O_3 and MgO, in that order. XRD of the solid products obtained after 70 min of reduction revealed MnO, Mn_5C_2, Mn metal, graphite and the respective catalysts. In the case of Na_2CO_3 traces of

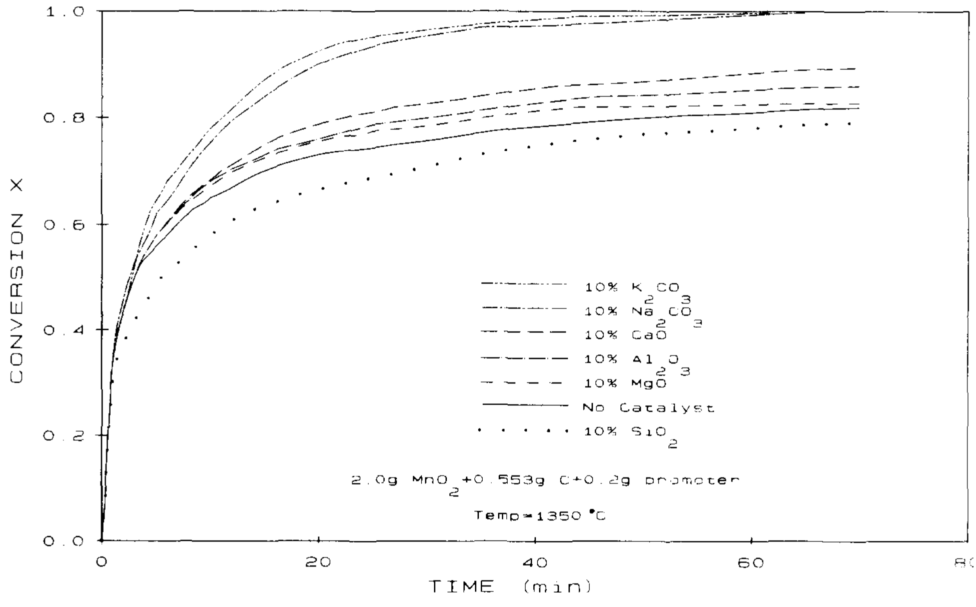

Fig. 1. Effect of catalysts on the reduction of MnO_2 by graphite at 1350 °C.

β-$NaMnO_2$ could be found. No other interactions between manganese oxides and these catalysts were indicated by the XRD patterns. Figure 1 shows that silica had an inhibiting effect on reduction kinetics, in spite of its accelerating effect on the Boudouard reaction [5]. XRD patterns in this case indicated the presence of β-$MnSiO_3$ in addition to β-quartz, Mn_5C_2, MnO and graphite. The slag β-$MnSiO_3$ could have coated some of the manganese oxide particles and thereby reduced their effective reaction area [5]. Similar results have been observed during the reduction of MnO [4,5]. It is also important to note that the carbide formed is Mn_5C_2 and not Mn_7C_3 as suggested by Grimsley et al. [2] and Downing [6].

XRD patterns after 1 min of reduction revealed Mn_3O_4, graphite and traces of MnO and γMn_2O_3. However, the XRD patterns of Mn_3O_4 and γ-Mn_2O_3 are much the same. XRD patterns after 2 and 5 min showed MnO, Mn_3O_4 and traces of Mn_5C_2. If the reaction mixtures considered in Fig. 1 were allowed to convert to Mn_5C_2 only, the maximum X value could be calculated theoretically to be 0.857. It can be seen that only CaO, Na_2CO_3 and K_2CO_3 yielded final X values which are higher than 0.857. It is therefore significant that the XRD patterns for MgO, Al_2O_3 and no catalyst after 70 min showed peaks of manganese metal which are much lower than those for CaO, Na_2CO_3 or K_2CO_3. In the case of Na_2CO_3 and K_2CO_3 the peaks for Mn_5C_2 are of very low intensity after 70 min. The MnO_2 seems to be reduced by graphite first to Mn_2O_3 then to Mn_3O_4 and MnO, followed by Mn_5C_2, which then reacts with the remaining MnO to form metallic manganese.

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