The oxidation kinetics of FeV_2O_4 in the range 200–580°C

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Abstract

The oxidation kinetics of FeV_2O_4 were studied using isothermal and non-isothermal methods of analysis. The isothermal experimental data are described in terms of the Jander equation with $E_a = 141$ kJ mol^{-1}. The non-isothermal analysis showed that the kinetics can be described in terms of three different overlapping processes. The first process, oxidation of the spinel to give a solid solution, is described in terms of a first-order nucleation mechanism, $E_a = 61$ kJ mol^{-1}, and take place in the temperature range 180–380°C. The second process, the oxidation of the solid solution, takes place from ≈ 360°C and is described by a diffusion mechanism with $E_a = 249$ kJ mol^{-1}. The third process, oxidation of the remaining spinel, is described by a first-order nucleation model with $E_a = 345$ kJ mol^{-1} and overlap with the second process. The reaction is completed at ≈ 580°C.

Keywords: Iron vanadate; Isothermal; Kinetics; Mechanism; Non-isothermal; Oxidation; Vanadate

1. Introduction

The solid state reactions occurring during the oxidation of the spinel FeV_2O_4 have been described previously [1]. The oxidation reaction

$$4FeV_2O_4 + 5O_2 = 4FeVO_4 + 2V_2O_5$$

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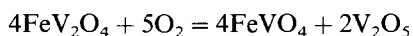
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was described in terms of three overlapping reactions. These reactions are exothermic and caused severe self-heating, of the sample with the result that the V_2O_5 which formed was heated to temperatures above its melting point. The molten V_2O_5 solidified as the reaction slowed down and formed a crust around the unreacted particles. This in turn reduced the availability of oxygen for further oxidation. This effect became noticeable at isothermal temperatures $> 470°C$ or when heating rates $> 5°C$ min^{-1} were used in dynamic runs.

The kinetics of oxidation of FeV_2O_4 were investigated by Ryzhov et al. [2]. They found that the spinel was incompletely oxidized and ascribed this fact to the formation of a solid solution between Fe_2O_3 and V_2O_3 and to the non-stoichiometry of the V_2O_3 starting material used in the preparation of the spinel. They used the linearity of the $\log[-\log(1-\alpha)]$ versus $\log(time)$ plots as a criterion in their kinetic studies. These plots are known to be insensitive to possible experimental errors and should only be used in preliminary kinetic studies. It was therefore of interest to reinvestigate the oxidation kinetics of FeV_2O_4. Isothermal and non-isothermal methods of analysis were used.

2. Experimental

2.1. Sample preparation

The method of Rogers was used to prepare the spinel, and has been described previously [1].

2.2. Thermal analysis

TG experiments were carried out on a Du Pont 990 thermal analyser with a 951 TG analyser unit. In all isothermal runs, the sample was inserted into the TG furnace only after the furnace had reached a predetermined temperature. The isothermal data were analysed by using a computer program based on the linearity of the $f(\alpha)$ versus time plot for a given kinetic function as the criterion to determine the kinetic function best describing the experimental data. The values of the correlation coefficient and the standard deviation were used to determine the best straight line. Only data collected in the range $360–460°C$ were used for kinetic analysis. This was necessary in order to eliminate the melting of V_2O_5 as described above. The TG data used for the non-isothermal kinetic analysis were recorded by heating a sample at a constant rate of 1 K min^{-1} in a dynamic oxygen atmosphere from room temperature to $600°C$. This relatively slow heating rate was used in order to overcome the problems of overheating and melting. The data were analysed using a computerized application of the Zsako method of analysis. This program and method of analysis were described recently [3].

DSC runs were recorded on a Perkin-Elmer DTA 1700 operated in the DSC mode. Platinum sample and reference cups were used.

All thermal analysis runs were recorded in a dynamic oxygen atmosphere with a flow rate of 50 ml min^{-1}. Sample sizes were between 35 and 40 mg per experiment.

3. Results and discussion

3.1. Isothermal kinetic analysis

The isothermal TG curves for oxidation of the spinel in the range 360–460°C are given in Fig. 1. The oxidation is incomplete after 20 h in this temperature range. The α vs. time curves were calculated by using the experimentally observed mass gain of 17.95% for complete oxidation of FeV$_2$O$_4$ to correspond with $\alpha = 1$.

The Jander equation $[1 - (1 - \alpha)^{0.33}]^2 = kt$, describing a three-dimensional diffusion process of a gaseous phase through a product layer, gave the best description of the experimental data. Table 1 summarizes the isothermal kinetic results. It is clear that the linearity of the plot of $[1 - (1 - \alpha)^{0.33}]^2$ vs. time decreases at isothermal temperatures above 400°C. Although this is the case, the Jander equation still gave the best description.

The Arrhenius equation with the rate constants listed in Table 1 is given by the equation

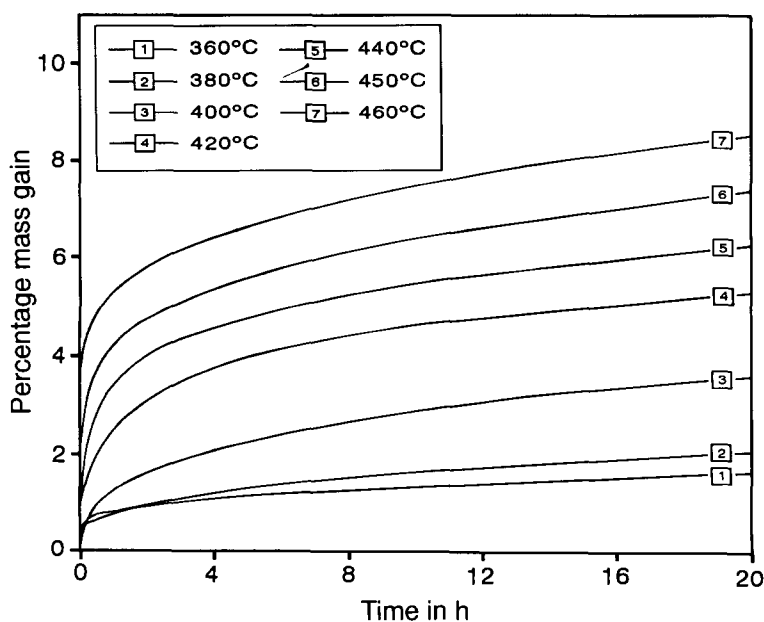$$\ln k = 12.73 - 1.69 \times 10^4 T^{-1}$$

Fig. 1. Isothermal TG curves for the oxidation of FeV$_2$O$_4$ in the range 360–460°C.

Table 1
Isothermal rate constant values for the oxidation of FeV_2O_4 as described by the Jander equation

Temp./°C	$k/(min^{-1})$	Corr. coeff.	Stand. dev.
360	8.06×10^{-7}	0.992	1.0×10^{-4}
380	1.20×10^{-6}	0.993	1.0×10^{-4}
400	5.40×10^{-6}	0.999	1.0×10^{-4}
410	8.40×10^{-6}	0.988	3.0×10^{-4}
420	1.02×10^{-5}	0.962	1.2×10^{-4}
440	1.44×10^{-5}	0.954	1.8×10^{-3}
450	1.98×10^{-5}	0.959	2.3×10^{-3}
460	2.88×10^{-5}	0.956	3.3×10^{-3}

The activation energy is therefore $E_a = 141$ kJ mol^{-1}, and the frequency factor $A = 3.38 \times 10^5$ min^{-1}. Simulation of isothermal curves using these kinetic parameters showed very poor correlation with the experimental data, indicating that the Jander equation for the overall reaction does not describe the process adequately. This method of analysis was subsequently abandoned.

3.2. Non-isothermal kinetic analysis

The non-isothermal curves of TG and DTA for the oxidation reaction using a heating rate of 5 K min^{-1} are illustrated in Fig. 2. The DTA curve shows that oxidation consists of at least three distinct processes. These processes have been described [1] and can be summarized as follows.
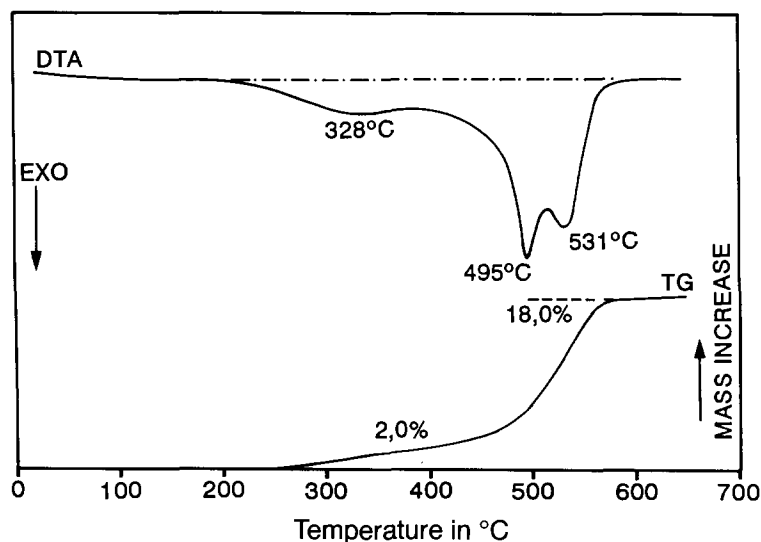

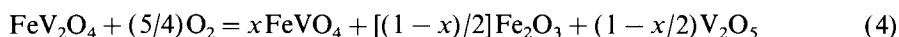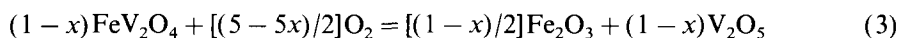Fig. 2. DTA and TG curves for the oxidation of FeV_2O_4 at a heating rate of 5 K min^{-1}.

(i) Oxidation of FeV_2O_4 to an R_2O_3 solid solution, consisting of α-Fe_2O_3 and V_2O_3, in the range ≈ 180–$380°C$.

(ii) Oxidation of the V(III) in R_2O_3 to V_2O_5 in the range ≈ 400–$470°C$. The V_2O_5 and Fe_2O_3 combine to form $FeVO_4$.

(iii) Oxidation of the remaining FeV_2O_4 to $FeVO_4$ and V_2O_5 through the formation of various suboxides of vanadium, e.g. V_6O_{13}, in the range ≈ 460–$600°C$.

The three processes overlap to some extent, especially the second and third processes. In order to give a meaningful description of the kinetics it was necessary to resolve the kinetic curve into three curves, each characteristic of a process.

If it is assumed that x is the fraction of spinel converted to the solid solution in the first process, then the following oxidation scheme can be constructed

$$x\,FeV_2O_4 + (x/4)O_2 = (3x/2)Fe_{2/3}V_{4/3}O_3 \tag{1}$$

$$(3x/2)Fe_{2/3}V_{4/3}O_3 + xO_2 = x\,FeVO_4 + (x/2)V_2O_5 \tag{2}$$

$$(1-x)FeV_2O_4 + [(5-5x)/2]O_2 = [(1-x)/2]Fe_2O_3 + (1-x)V_2O_5 \tag{3}$$

$$FeV_2O_4 + (5/4)O_2 = x\,FeVO_4 + [(1-x)/2]Fe_2O_3 + (1-x/2)V_2O_5 \tag{4}$$
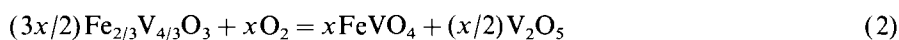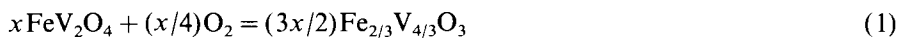
Theoretically, each of the reactions (1), (2) and (3) will have its own set of kinetic parameters, activation energy and frequency factor, and will be described by an unique kinetic model $f(\alpha)$. This would mean that the total mass gain in terms of fractional oxidation (reaction (4)) can be represented by the equation

$$\alpha_{total} = p_1\alpha_1 + p_2\alpha_2 + p_3\alpha_3$$

where α_1, α_2 and α_3 are the fractional decompositions of the individual reactions calculated from the kinetic models describing reactions (1), (2) and (3) respectively; p_1, p_2 and p_3 are empirical constants derived from the fractional contributions due to reactions (1), (2) and (3); $p_1 + p_2 + p_3 = 1$, with $p_1 = 3.61x/18.04$, $p_2 = 14.43x/18.04$ and $p_3 = 1 - x$

The formation of the R_2O_3 solid solution, reaction (R1), accounted for $\approx 11\%$ of the total mass gain which was observed for the oxidation of the spinel; see Fig. 2. A value of 0.11 was therefore used for p_1 and a subsequent value of 0.55 for x. This means that $\approx 55\%$ of the spinel is converted to the solid solution before the other oxidation reactions start to take place. This value of p_1 implies that p_2 and p_3 have values of 0.44 and 0.45 respectively. Using these values for x, p_1, p_2 and p_3 and the computer software [3], analysis of the non-isothermal TG curve based on the chemistry described previously [1] gave the results shown in Table 2. Fig. 3 shows the three individual simulated kinetic curves. The total of these three curves, curve 4, gives an excellent description of the experimental data, as is illustrated in Fig. 3.

3.3. The mechanism of oxidation

FeV_2O_4 is oxidized to the solid solution according to a kinetic model describing a random nucleation process. The activation energy of the process is relatively low,

Table 2
Kinetic parameters describing the oxidation of FeV_2O_4

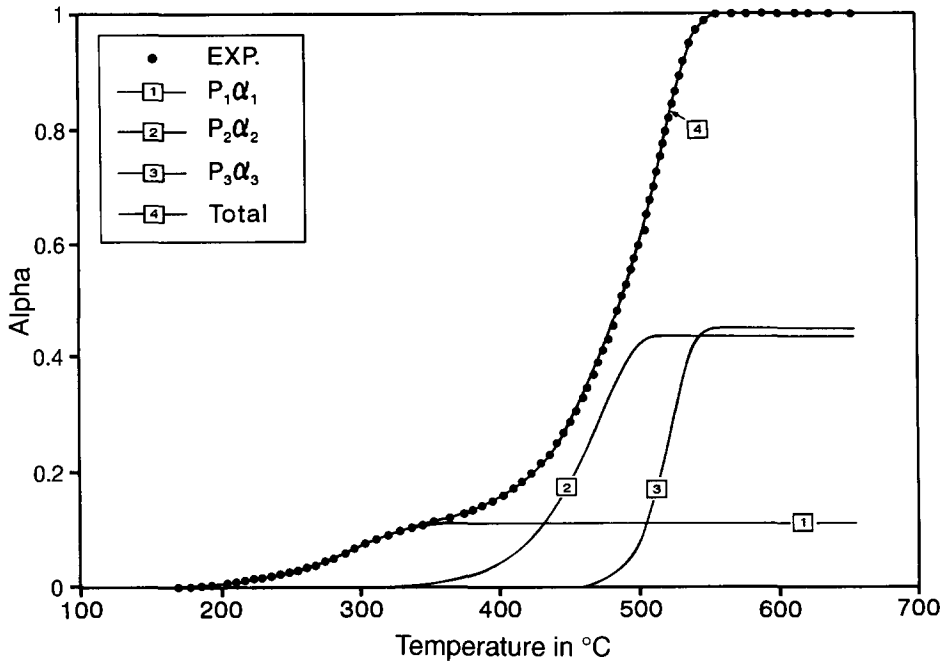| Reaction	Kinetic model	Activation energy/(kJ mol^{-1})	$\ln(A/min^{-1})$
(R1)	$-\ln(1-\alpha) = kt$ (first order)	61	9.15
(R2)	$[1-(1-\alpha)^{0.33}]^2 = kt$ (Jander)	249	34.96
(R3)	$-\ln(1-\alpha) = kt$ (first order)	345	49.33

Fig. 3. Experimental and calculated non-isothermal TG curves at a heating rate of 5 K min^{-1}.

61 kJ mol^{-1}, and it is therefore postulated that the spinel particles are rapidly covered with a product layer consisting of the solid solution. During the second kinetic process, which overlaps only to a small extent with the first process, the R_2O_3 is oxidized to V(V) oxides according to the Jander three-dimensional diffusion mechanism. The third kinetic process, which is mainly the oxidation of the unreacted spinel through suboxides such as FeV_2O_6 and V_6O_{13}, is described by a first-order nucleation model and is complete at 580°C. This process overlaps to a large extent with the second process.

The results illustrate that the proposed mechanism of oxidation and the obtained kinetic parameters are in good agreement with the experimental data.

4. Conclusions

The oxidation kinetics of the spinel FeV_2O_4 can be described in terms of three individual kinetic processes. These processes overlap to some degree, but a careful consideration of the chemistry of the process, and the application of a computerized version of the Zsako method of analysis, allowed the calculation of the kinetic parameters of the various processes.

References

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