Thermoanalytical study of the reaction of potassium carbonate with ferric oxide

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Abstract

The reaction of potassium carbonate with ferric oxide was investigated thermogravimetrically. Both non-isothermal and isothermal conditions were used for the kinetic study of this reaction. The reaction between K_2CO_3 and Fe_2O_3 yields $KFeO_2$ and the reaction occurs at lower temperature than the decomposition temperature of pure K_2CO_3. Arrhenius parameters were derived from the experimental data and a reaction mechanism for the formation of $KFeO_2$ is proposed. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The reactions between alkali metal carbonates and oxides of iron, nickel and cobalt are of interest because of their relevance in molten carbonate fuel cell technology [1]. Molten alkali metal carbonates also find use as electrolytes in electrochemical meters for measuring carbon activity in liquid alkali metals [2–4]. In these meters, molten electrolytes are contained in either iron or nickel capsules. Oxygen partial pressure over the electrolyte as well as the surface conditions of the capsule material (e.g., presence of the oxide layer) is found to influence the performance of these meters significantly [4]. A knowledge of the kinetics of the reactions between iron or nickel oxides, and the carbonates of lithium, sodium and potassium is essential to understand the processes that take place in the electrochemical cells. Data on reactions between Na_2CO_3 and Fe_2O_3 and Li_2CO_3 and Fe_2O_3 were reported by Colovic et al. [5] and Gallagher and Johnson [6]. This paper deals with our investigations aimed to derive data on the kinetics of the reaction between K_2CO_3 and Fe_2O_3.

2. Experimental

An equimolar mixture of potassium carbonate (Suprapure grade, M/s Merck, India) and ferric oxide (99.9%, M/s Fisher Scientific, USA) was homogenised, dried, pelletised and oven dried. Thermogravimetric measurements were carried out using Rheometric Scientific STA 1500 instrument, which had a sensitivity of 1 μg in the mass range employed and a dynamic oxygen atmosphere with oxygen flowing at a rate of 50 ml min^{-1} was maintained over the samples. Recrystallised alumina crucible was used as

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sample container and α-alumina as the reference material. Both isothermal and programmed heating runs were performed using sample pellets of approximately 25 mg mass. Isothermal experiments were carried out at 873, 898, 923, 973, and 998 K. Experiments under non-isothermal conditions were carried out at programmed heating rates of 1, 2, 5, 10 and 20 K min^{-1}. Experiments under non-isothermal conditions were carried out with pure K_2CO_3 also at all heating rates. The product obtained after carrying out the thermogravimetric experiments with an equimolar mixture of K_2CO_3 and Fe_2O_3 was characterised by using a Siemens 800 X-ray diffractometer utilising CuKα radiation. The temperature calibration was carried out by fixed melting point method using ICTAC recommended standards like indium, tin and gold.

3. Results and discussion

The thermogravimetric curves of pure $K_2CO_3 \cdot 1.5H_2O$ and equimolar mixture of K_2CO_3 and Fe_2O_3 are shown in Fig. 1. Three weight loss processes were observed with $K_2CO_3 \cdot 1.5H_2O$ starting at 353, 425, and 1173 K. The processes that occur below 473 K are due to loss of adsorbed moisture and loss of water of hydration. (The weight loss below 473 K are not shown in Fig. 1.) K_2CO_3 starts decomposing at ca. 1173 K and the decomposition is complete by 1413 K. However, as seen from Fig. 1, in the presence of Fe_2O_3 decomposition of K_2CO_3 occurs at well below 1173 K. The reaction between equimolar mixture of K_2CO_3 and Fe_2O_3 is represented as

$$K_2CO_3 + Fe_2O_3 \rightarrow 2KFeO_2 + CO_2 \qquad (1)$$

From the weight loss measurements, the product formed from the reaction between equimolar mixture of the starting materials was inferred as $KFeO_2$. XRD pattern of the product obtained, shown in Fig. 2, confirmed it to be $KFeO_2$ (JCPDS pattern no. 26-1319i). From the thermogravimetric curves of the reaction (1), the fraction reacted, α, was evaluated as a function of time or temperature. Fig. 3 shows variation of α with time t for different heating rates. It is observed that the α–t relationship is sigmoidal in nature.

The reaction rate for non-isothermal and isothermal methods can be represented as given below:

$$d\alpha/dT = (k/\beta)f(\alpha) \quad \text{(non-isothermal)}, \qquad (2)$$

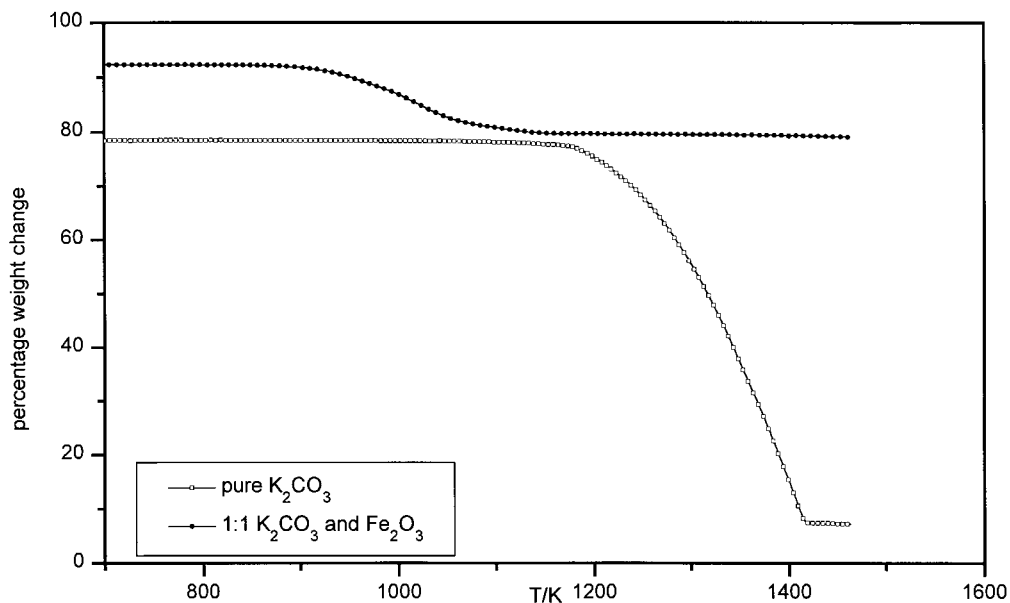$$d\alpha/dt = kf(\alpha) \quad \text{(isothermal)}, \qquad (3)$$

Fig. 1. Thermogravimetric curves of pure K_2CO_3, 1:1 molar ratio of K_2CO_3 and Fe_2O_3 at a heating rate of 5 K min^{-1} in flowing oxygen.
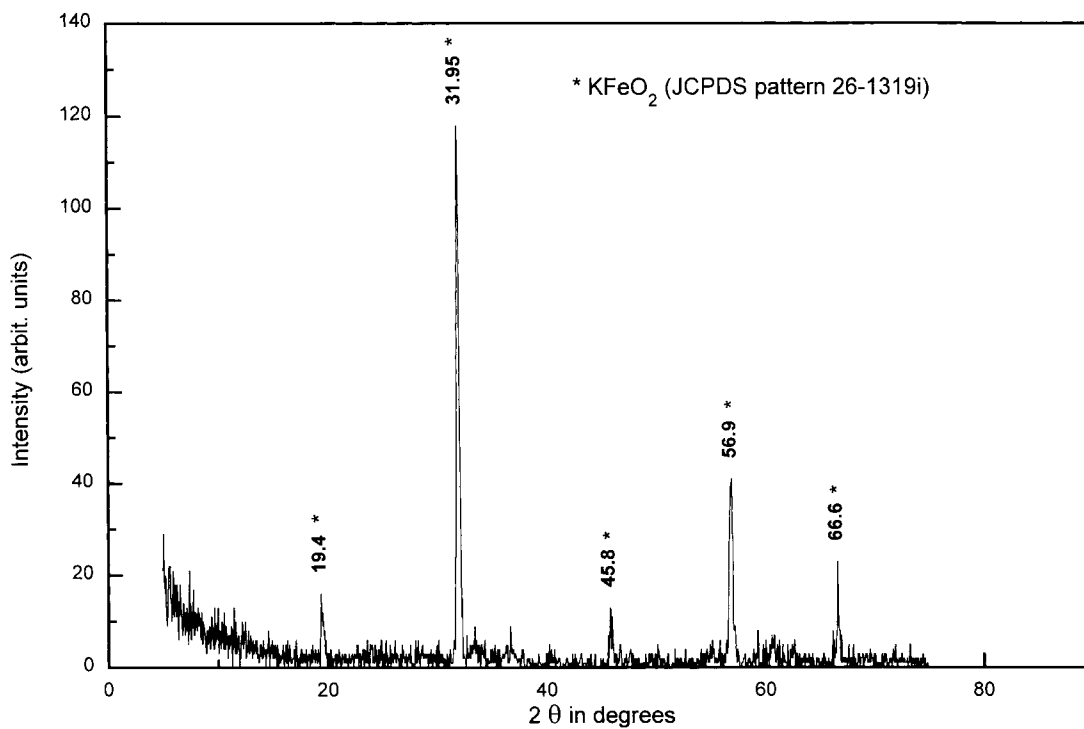
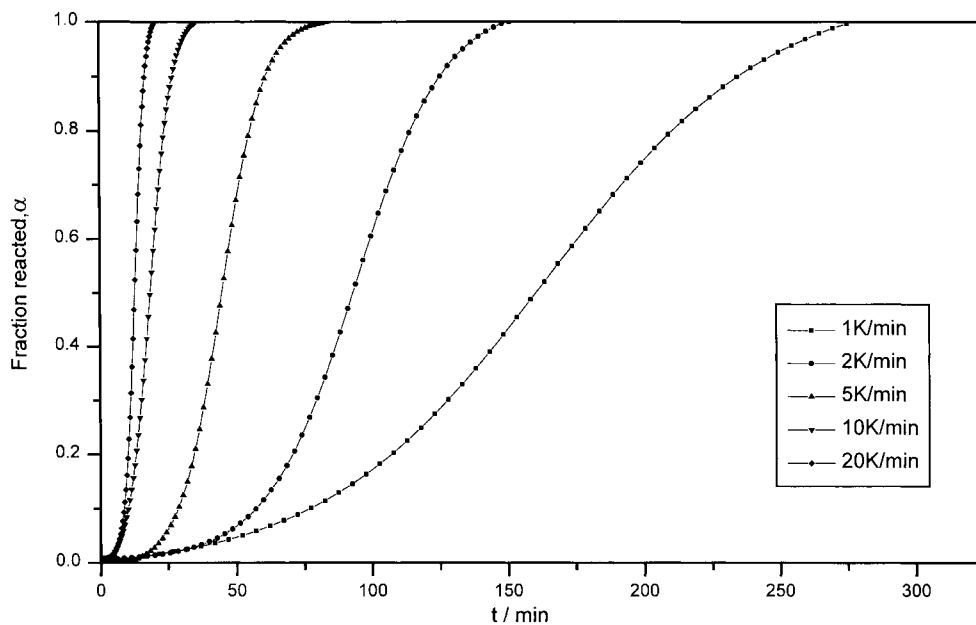Fig. 2. XRD pattern of reaction product between K_2CO_3 and Fe_2O_3.

Fig. 3. Fraction reacted (α) as a function of time in minutes for the reaction of K_2CO_3 with Fe_2O_3 at different heating rates.
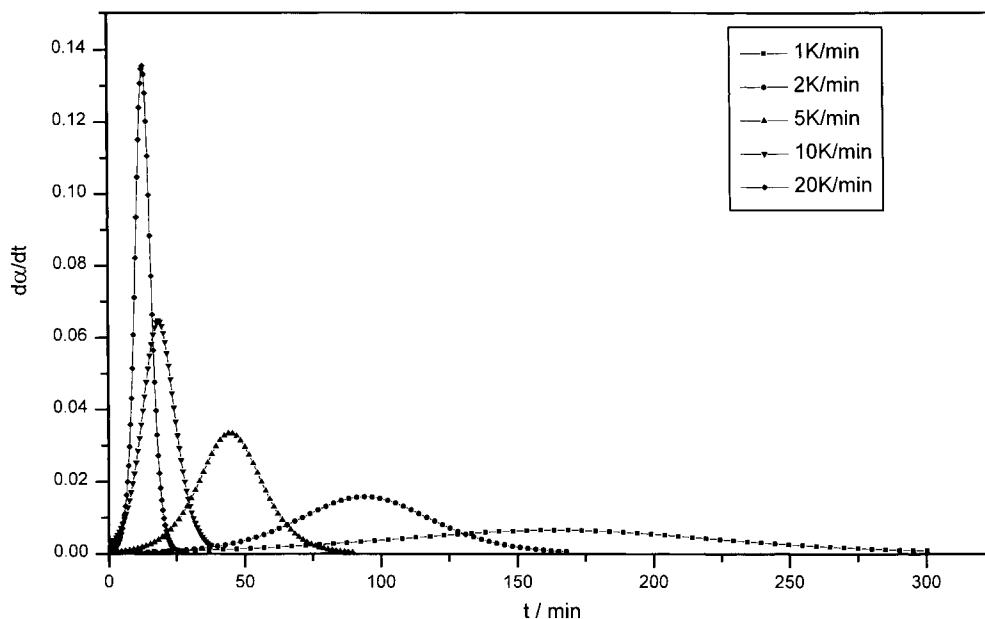
Fig. 4. First derivative curve of α as a function of time for the reaction between K_2CO_3 and Fe_2O_3 at different linear heating rates.

where k is the rate constant, β the programmed heating rate and $f(\alpha)$ is the function of α which depends on the mechanism of the thermal process. Rate constant, k, is assumed to follow Arrhenius equation, $k = A \exp(-E/RT)$ where A is the pre-exponential factor and E is the activation energy.

For evaluation of the data from non-isothermal technique, a method independent of any physical model as well as a method based on physical model were employed. Analysis of the data by the physical model independent method involved numerical differentiation of the curves representing variation of α as a function of time obtained at various linear heating rates, the results of which are shown in Fig. 4. From these kinetic curves, maximum reaction rate (V_{max}), the corresponding temperature (T_{max}), and the treatment time (t_{max}) were obtained and kinetic

parameters were deduced using the following Eqs. (4)–(6) [5,7,8].

$$\mathrm{d} \ln V_{max}/\mathrm{d}(1/T_{max}) = -E/R, \qquad (4)$$

$$\mathrm{d} \ln t_{max}/\mathrm{d}(1/T_{max}) = E/R, \qquad (5)$$

$$\mathrm{d} \ln \beta/\mathrm{d}(1/T_{max}) = -E/R. \qquad (6)$$

Fig. 5. shows the plot of $\ln V_{max}$, $\ln t_{max}$, and $\ln \beta$ as a function of $1/T_{max}$. The values of activation energies and pre-exponential factors obtained from the plots are given in Table 1. The activation energies for the reaction between Na_2CO_3 and Fe_2O_3 were deduced in a similar manner by Colovic et al. [5] as 300, 249 and 278 kJ mol^{-1}, respectively. The authors reported the pre-exponential factors as $\log A$ (min) = 14.57 and 10.34.

Analysis of the data from non-isothermal technique by the physical model dependent method involved

Table 1
Kinetic parameters obtained from non-isothermal experimental data by applying a physical model independent method

Activation energy (kJ mol^{-1})			Pre-exponential factor $\log A$ (min)	
From Eq. (4) 218 ± 9	From Eq. (5) 192 ± 24	From Eq. (6) 221 ± 15	From Eq. (4) 52 ± 2	From Eq. (5) 44 ± 7

Fig. 5. Plot of $\ln V_{max}$, $\ln t_{max}$, $\ln \beta$ versus $1/T_{max}$.
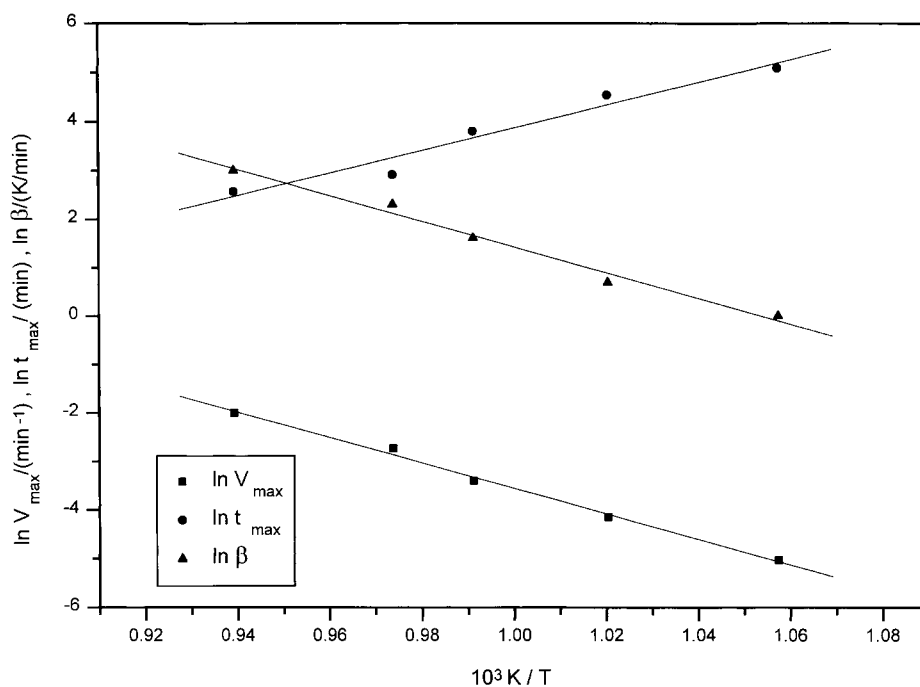
evaluation of the integral form of Eq. (2), which is represented as follows:

$$\int_0^\alpha d\alpha/f(\alpha) = g(\alpha) = \int_0^T (A/\beta)e^{-E/RT} \, dT,$$

(7)

where $g(\alpha)$ is the integral form of $1/f(\alpha)$. Coats–Redfern method (integral method) [9] was adopted using the various forms of $g(\alpha)$ reported in the literature [10] to identify the correct form of either $f(\alpha)$ or $g(\alpha)$ to be used for analysis of the experimental data, and to deduce the most probable reaction mechanism.

Out of all the $g(\alpha)$ functions, only Avrami–Erofe'ev A2 function, where $g(\alpha) = [-\ln(1-\alpha)]^{1/2}$, gave the best linear fit. Plots of $\ln[g(\alpha)/T^2]$ versus $1/T$ for the heating rates of 1, 2, 5, 10, and 20 K min^{-1} is shown in Fig. 6. Activation energies and the pre-exponential factors were evaluated using Coats–Redfern equation in the range of $\alpha = 0.1$–0.9 for various heating rates, and the results obtained are listed in Table 2. As the Avrami–Erofe'ev A2 mechanism involves two-dimensional nucleation and growth process, it is postulated that the reaction between K_2CO_3 and Fe_2O_3 involves

Table 2
Kinetic parameters evaluated using method based on Avrami–Erofe'ev A2 model (Coats and Redfern integral method)

Heating rate (K min^{-1})	α range	E (kJ mol^{-1})	log A (min)
1	0.1–0.9	55 ± 1	0.84 ± 0.04
2	0.1–0.9	74 ± 1	2.09 ± 0.06
5	0.1–0.9	64 ± 1	1.78 ± 0.08
10	0.1–0.9	64 ± 1	1.98 ± 0.06
20	0.1–0.9	73 ± 1	2.62 ± 0.06

nucleation and growth of $KFeO_2$. As seen in Table 2, the activation energy and the pre-exponential factor of this process lie in the range of 55–73 kJ mol^{-1} and 7–417 min^{-1}, respectively. From similar experiments, Gallagher and Johnson [6] deduced that the reaction between Li_2CO_3 and Fe_2O_3 follows either Jander or Ginstling–Brounshtein diffusion controlled mechanism with the activation energy of 209 and 176 kJ mol^{-1}, respectively.

Activation energies for the reaction between K_2CO_3 and Fe_2O_3 deduced from the non-isothermal experimental data by applying physical model independent method (Eqs. (4)–(6)) are higher than the values
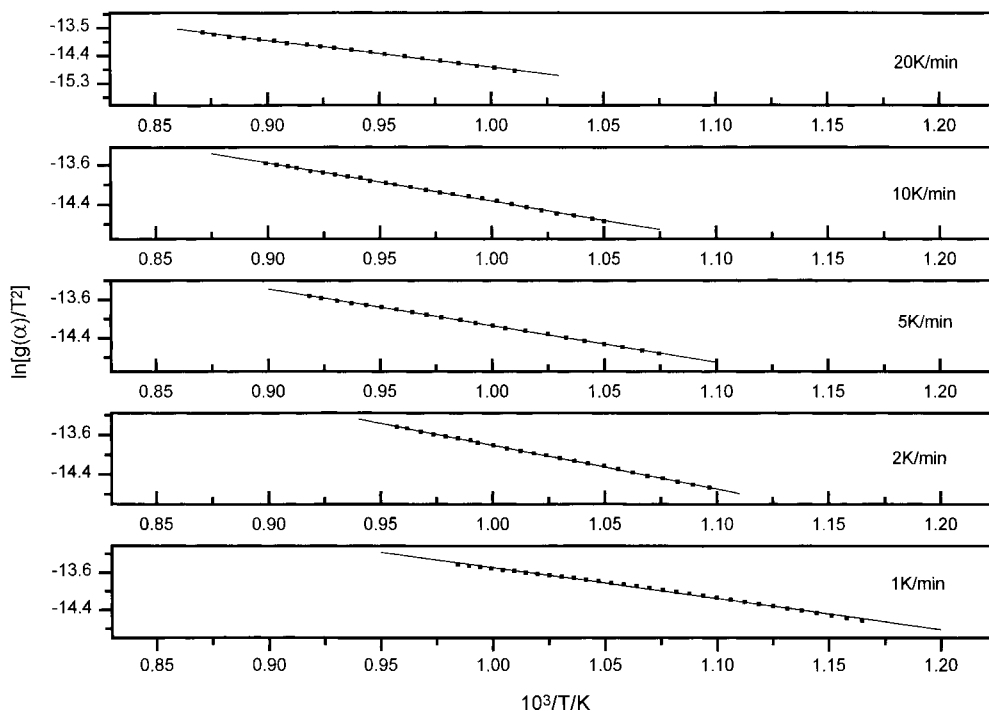
Fig. 6. Plot of Coats and Redfern integral equation for heating rates 1–20 K min^{-1}.

derived from the same data by adopting a physical model based treatment. With a view to investigate the system further, isothermal experiments were carried out. These isothermal experimental data obtained at 873, 898, 923, 973 and 998 K were evaluated by using the integral form of the Eq. (3):

$$g(\alpha) = kt. \tag{8}$$

Various forms of $g(\alpha)$ reported in the literature [10] were used in Eq. (8) to identify the correct mechanism by the linear fit method. As in the case of non-isothermal experiments, best linear fit was obtained with Avrami–Erofe'ev A2 $g(\alpha)$ function. Plots of $[-\ln(1-\alpha)]^{1/2}$ versus t is shown in Fig. 7 for data obtained at 873, 878, 973 and 998 K. By using Eq. (8), rate constant k at different experimental temperatures was obtained (Table 3). Using Arrhenius equation, activation energy and pre-exponential factor were obtained as 86 ± 9 kJ mol^{-1} and $12 \pm 4 \times 10^{-3}$ min^{-1} (see Fig. 8). Colovic et al. [5] derived the activation energies for the reaction between Na_2CO_3 and Fe_2O_3 from their non-isothermal experimental data by applying the physical model

Table 3
Values of rate constant k (min^{-1}) at various isothermal temperatures

T (K)	$k \times 10^4$ (min^{-1})
873	123.5 ± 3.4
898	141.0 ± 4.6
923	179.7 ± 2.8
973	344.9 ± 4.2
998	542.9 ± 9.9

independent method only. Hence a similar comparison of the difference in results obtained by treating the non-isothermal experimental data by both physical model dependent and independent methods was not possible. However, data from both non-isothermal and isothermal experiments of the present work show that the reaction between K_2CO_3 and Fe_2O_3 follow the mechanism involving a two-dimensional nucleation and growth process. Activation energy derived from the two sets of the experiments are also fairly in good agreement with each other supporting the inference about the reaction mechanism.
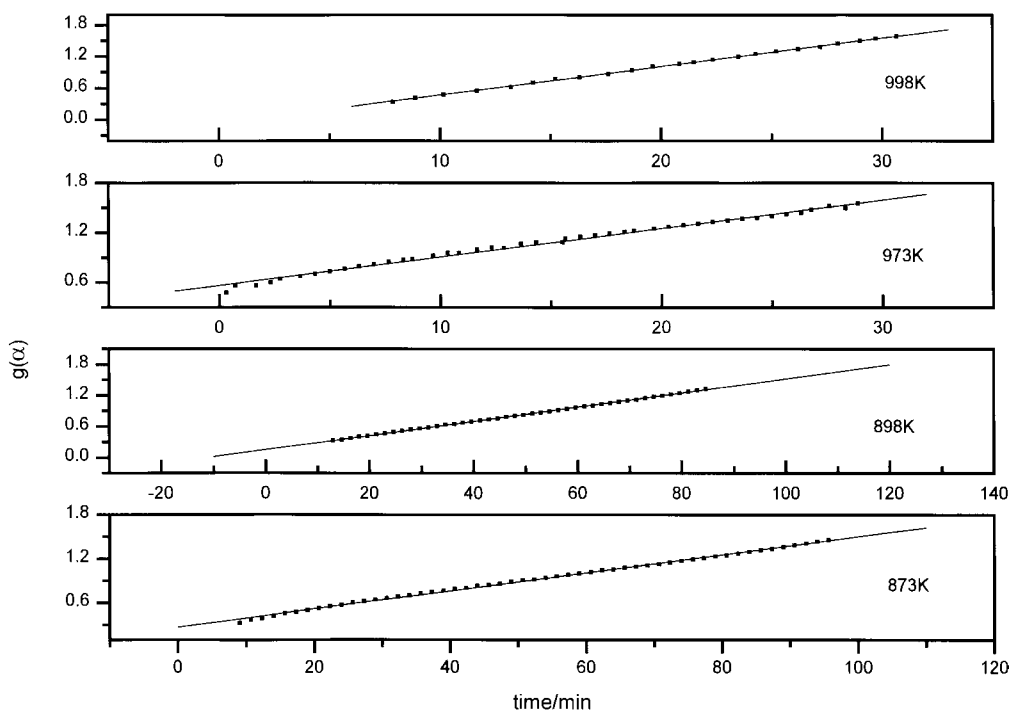
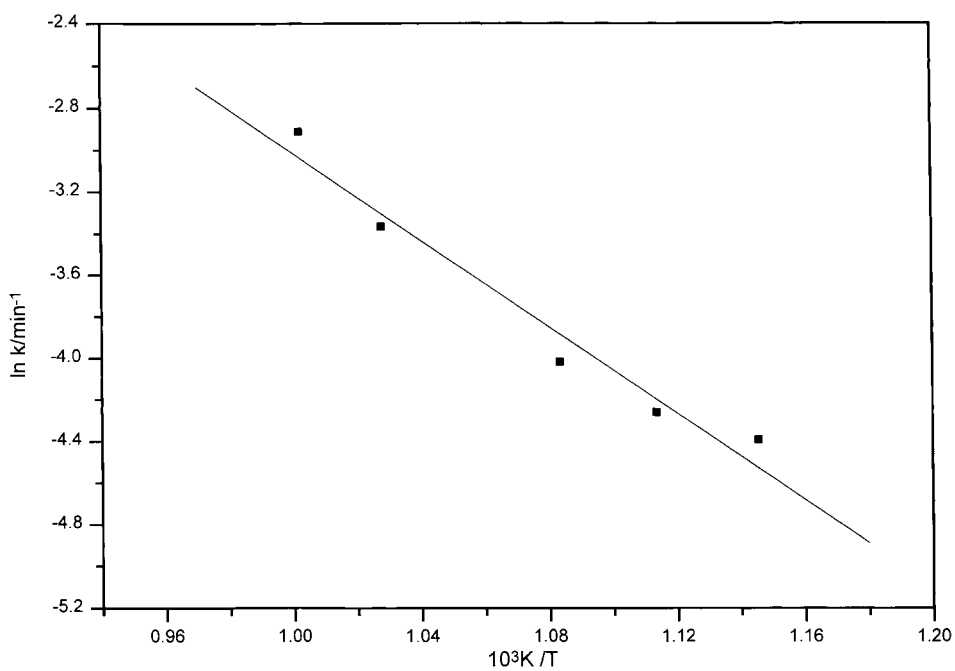Fig. 7. Plot of $g(\alpha)$ versus time at 873–998 K

Fig. 8. Arrhenius plot for the reaction between equimolar mixture of K_2CO_3 and Fe_2O_3.

4. Conclusions

The reaction between K_2CO_3 and Fe_2O_3 was studied thermogravimetrically under non-isothermal and isothermal conditions. The reaction of K_2CO_3 with Fe_2O_3 occurs at a lower temperature than the decomposition temperature of pure K_2CO_3. The product of the reaction was confirmed as $KFeO_2$ by XRD. Kinetic parameters were evaluated from the experimental results obtained under non-isothermal conditions by a method independent of physical model as well as a physical model based method. Kinetic parameters were also deduced from the results obtained under isothermal conditions. The parameters deduced from the isothermal experimental data are comparable to those deduced by a method based on a physical model from non-isothermal experimental data. It is proposed that the kinetics of the reaction between K_2CO_3 and Fe_2O_3 involves a two-dimensional nucleation and growth mechanism.

Acknowledgements

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