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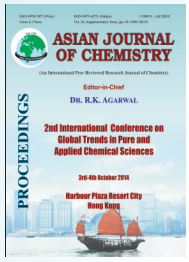

Calcination Kinetics of Phosphate Rock in CO_2 Atmosphere

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This study, examined the calcination of phosphate rock in fluidized bed, the effects of gas flow rate, temperature, particle size, calcination time and the rate of CO_2 on the decomposition rate. Calcination rate was observed to increase with increasing gas flow rate and temperature, but decreased with increasing particle size and CO_2 ratio in the fluid gas medium. Moreover, phosphate rock calcination was detected to conform to the unreacted core model among the heterogeneous reaction models. Both the fact that particle size is much more effective and the results of the Arrhenius equality support the transfer mechanism from ash film. In addition, the fact that the flow rate of the gas is very much effective suggests that the controlled transfer mechanism from fluid film affects the calcination as well. However, it can be proposed that the step which determines the velocity of the calcination reaction is the mass transfer controlled mechanism of CO_2 in the ash film with 31.08 kJ/mol activation energy.

Keywords: Phosphate rock, Calcination, Kinetics, Modeling.

INTRODUCTION

In order for the people to eat food and for the agricultural needs to be met, agricultural products should be increased to the required level in proportion to the increasing population. More than half of the world's population is facing malnutrition and hunger exacerbates the importance of the issue[1].

Fertilizers are known to be the most important factor in increasing the yield of agricultural products. In recent years, due to the increasing demand for high quality fertilizers, phosphate rock is used in large amounts for the production of phosphoric acid[1].

Grades for phosphate rock are usually given as P_2O_5 (phosphorus pentoxide) and depending on the amount of P_2O_5, they are divided into three groups as low-grade ores (12-16 %), medium-grade ores (17-25 %) and high-grade ores (26-35 %)[2].

Phosphoric acid is obtained by treatment of phosphate rock with a strong acid. Often, sulfuric acid is used for this purpose because of its inexpensiveness. The following reaction takes place in the production of phosphoric acid:

$$CaF_2{\cdot}3Ca_3(PO_4)_2 + 10H_2SO_4 + 20H_2O \longrightarrow 6H_3PO_4 + 10CaSO_4{\cdot}2H_2O + 2HF \quad (1)$$

The function of sulfuric acid in this reaction is to precipitate the calcium ions in the reaction medium as gypsum and to form the phosphoric acid by providing the necessary protons[3].

In order for the phosphate rock to be used in the production of phosphoric acid, its P_2O_5 content is required to be more than 26 %. Therefore, phosphate rock is subjected to enrichment process before it is used in the production of phosphoric acid. Breaking, gravitational methods, or flotation can be used for this purpose. The major gangue compounds found in the phosphate rock are generally clays, quartz and limestones[3,4].

Clays can easily be removed by washing the phosphate rock. Gravitational methods, electrostatic separation and flotation can be applied for removing other gangue compounds. However, in order to apply these methods, initially, a size reduction process must be applied on the ore so that minerals become free particles. In carbonated phosphates, carbonates are distributed in the medium quite homogeneously and so as to have a very small phase size. Moreover, sometimes they might have formed intermediate compounds with phosphates. Therefore removing carbonate minerals is either too expensive or difficult, or not economically feasible with the current technology. Therefore, the above-described physical enrichment methods are not applicable with a good yield. Calcination process is applied on such ores for enrichment purposes[5].

The first incident is drying in calcination when the temperature rises. This is followed by combustion of organic matter, decomposition of carbonates (dissociation) and elimination of CO_2. Decomposition of carbonates such as

dolomite, magnesite and calcite is simply demonstrated as follows:

$$CaMg(CO_3)_2 \rightleftharpoons CaCO_3 + MgCO_3 \quad (2)$$

$$MgCO_3 \rightleftharpoons MgO + CO_2 - Q \quad (3)$$

$$CaCO_3 \rightleftharpoons CaO + CO_2 - Q \quad (4)$$

Decomposition of carbonates starts at 500-600 °C and accelerates with increasing temperature[6].

Decarbonization finishes at 900 °C and this temperature is 50 °C below the sintering temperature. Calcination depends on parameters such as particle size, reaction time, gas phase, type of furnace where calcination is carried out and the ratio of silicates. The calcination process is carried out at high rates regardless of the amount of carbonate available. Decomposition of carbonates, elimination of CO_2, elimination of organic materials and the removal of crystalline water take place in the calcination process[7].

Enrichment with calcination process is applied in three steps *i.e.*, pre-treatment, calcination and the final-treatment. In pre-treatment, generally, the gangue minerals are removed. With the removal of gangue minerals before calcination, the heat required for heating, decomposition and temperature-dependent chemical reactions of these minerals is saved. The fact that vitreous materials, which form as a result of chemical reactions of these gangue minerals at calcination temperature, lead to the loss of significant amounts of phosphate and bind crystals to each other prevents the targeted enrichment. Therefore, pre-treatment is required for most of the phosphate ores. In the final treatment, the aim is to remove the existing calcium oxide and magnesium oxide from the calcined ore[8].

In this study, it was aimed to investigate the effects of furnace atmosphere on the calcination of the Mazidagi (Turkey) phosphate ore under fluidized bed conditions. Air containing various amounts of CO_2 was used for this purpose. Initially, experiments were conducted in a medium devoid of CO_2 for comparison purposes and the results were interpreted accordingly.

EXPERIMENTAL

Phosphate ore used in this study wasprovided from the phosphatedeposits in Mazidagi. Thesample was crushed, ground and then sieved to give 250-355, 355-500, 500-710 and 710-1000 μm size fractions using ASTM standard sieves. The chemical analysis ofthe phosphate rock was carried out by standard gravimetric, volumetric and spectrometric methods and the results of chemicalanalysis of the sample are given in Table-1.

A schematic diagram of the experimental setup is shown in Fig. 1. Experiments were performed in a fluidized-bed reactor, which consisted of quartz (3 cm inner diameter) with a gas preheating section below the distributor. It was heated by positioning the tubular electric furnace centrally. A chromel-alumel thermocoupleand a temperature controller were used to control the temperature of the bed. The reacting gas was prepared by mixing 2-15 % CO_2 and the rest being air. As the fluidization medium, sand (15 g) with 250-300 μm particle size was added to the reactor through the top of the reactor. To minimize variations in the bed temperature and to achieve the differential conditions, a minimum practical quantity of phosphate rock (approximately 1 g) was used. The temperature of the bed was raised and kept for 10 min at the desired level, before charging the phosphate rock sample from the top of the bed. At the end of the calcination, the sample was discharged by applying vacuum and was collected in the sample hold up. Samples of dust and fine particles were recovered using two cyclones connected to this sample hold up. The sand was separated by sieving from partially calcined phosphate samples. After calcination, the samples were stored in an airtight bottle. Silica gel crystals were added to the bottle to absorb any moisture during the storage.

TABLE-1
CHEMICAL ANALYSIS RESULTS OF THE PHOSPHATE ROCK

Components	Percentages
CaO	51.10
P_2O_5	21.48
MgO	1.49
Fe_2O_3	0.40
Al_2O_3	1.21
SiO_2	0.85
F_2	2.59
Loss on ignition (CO_2)	20.75 (17.58)
Cannot be determined	0.13

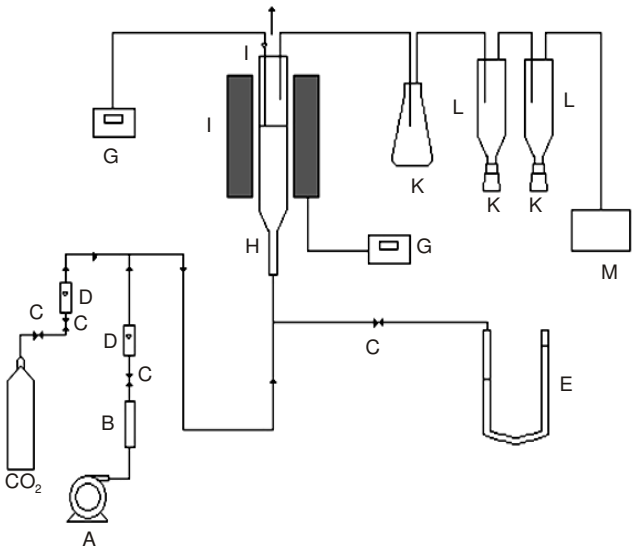

Fig. 1. Schematic diagram of experimental setup; (A) Air compressor, (B) Dryer, (C) Control valve, (D) Flow meter, (E) Manometer, (G) Temperature controller, (H) Preheating column, (I) Reactor, (J) Thermocouple, (K) Sample hold up, (L) Cyclone, (M) Vacuum pump, (N) Gas out

Partially calcined phosphate samples were weighed and then completely calcined in a muffle furnace for 2 h at 900 °C. The complete calcined samples were again weighted. Since the complete calcination conversion of the phosphate rock is known, the calcination conversion in fluidized bed is calculated from eqn. 5.

Calc. conversion in fluidized bed (%) = [(Complete calc. conversion – Calc. conversion inmuffle furnace)/Complete calc. conversion] × 100 (5)

Each experiment was repeated 3 times and the average of the results of these experiments was used in the calculation of the calcination conversions.

RESULTS AND DISCUSSION

In this study, the effects of gas flow rate, temperature, particle size, calcination time and gas composition parameters on the calcination of phosphate rock were investigated.

Effect of gas flow rate: In order to determine the effect of gas flow rate on the calcination of phosphate ore at constant temperature, samples with particle size of 355-500 μm were processed at 800 °C. In this experiment, a synthetic CO_2-air mixture was used; this mixture contained 15 % CO_2 and rest being air was appropriate for the gas atmosphere in furnaces which were generally used for direct heating. Initially, empirical experiments were conducted for the minimum fluidization velocity (Umf) and consequently, the minimum fluidization velocity was determined to be 8.25 cm/s at 800 °C. In the experiments, 1, 2, 4, 6, 8 and 10 times of minimum fluidization velocity was used; *i.e*., minimum fluidization velocities of 8.25, 16.5, 33, 49.5, 66 and 82.5 cm/s were used and the data of the 15th min in the calcination when the equilibrium was reached were demonstrated in Fig. 2. Velocities higher than 82.5 cm/s could not be implemented due to the movement of particles outside the experiment medium. As can be observed in the Fig. 2, conversion is slow at velocities lower than 33 cm/s. On the other hand, conversion is higher at velocities higher than 49.5 cm/s and there is almost no difference between the conversion rates beyond this threshold. According to these results, it was decided to work at a constant flow rate of 49.5 cm/s in further experiments.

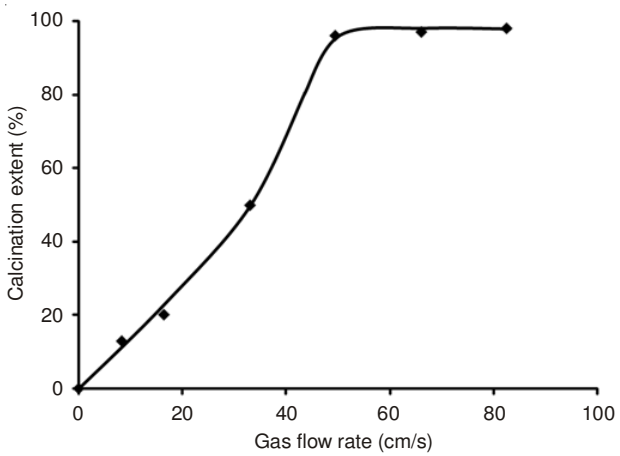

Fig. 2. Effect of gas flow rate as a function of time on the calcination of particles in the 355-500 μm intervals at 800 °C

When a solid particle comes in contact with a fluid, the surface of the solid particle is covered with a film formed of the stagnant fluid. This is called the boundary layer[9]. This concept is used to explain transfer events and reactions between phases in all heterogeneous systems such as gas-solid or liquid-solid systems. The presence of such a stagnant layer on the surface of the particles makes the convection events such as the transfer of heat and mass difficult. In other words, it constitutes a resistance to convection. In convection events, the resistance also increases as the thickness of this layer increases. In fluid-solid reactions, when the relative velocity between the fluid and the solid increases, the thickness and the resistance of this layer decreases[10].

Fig. 2 displays the effect of the fluid velocity on calcination that the rate of decomposition increases with increasing gas flow rate. In other words, gas flow rate significantly affects the conversion rate. This situation can be explained by the decrease in gas film resistance against the convection event with the increasing gas flow rate. Accordingly, it can be suggested that the calcination event takes place according to a transfer-controlled mechanism from the fluid film under the conditions of this experiment.

Effect of temperature: In order to determine the effect of temperature on calcination of phosphate ore at constant air flow rate of 49.5 cm/s, particles of 355-500 μm were processed for various durations at 700, 750, 800, 850 °C. Calcination results were displayed in Fig. 3. When the curves displayed in the Fig. 3 were analyzed, it was observed that calcination velocity was sensitive to temperature and the maximum conversion rate increased with increasing temperature. The reaction reached the steady state in the 15th minute at almost all temperatures and a high yield was obtained. A conversion rate of 100 % was reached at the highest temperature used in the experiments, *i.e*., at 850 °C. However, the fact that the conversion obtained at all temperatures led to lower yields when compared to the results obtained with fluid velocity suggests that decomposition event is not chemical but transfer-controlled[10,11].

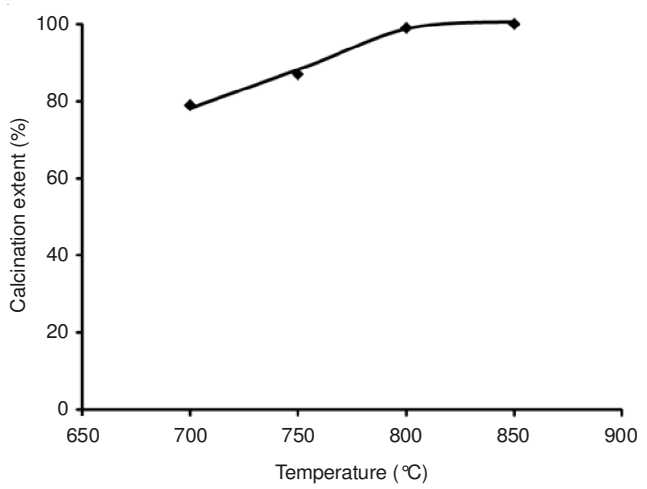

Fig. 3. Effect of temperature as a function of time on the calcination of particles in the 355-500 μm intervals

Effect of particle size: In order to determine the effect of particle size on the calcination of the phosphate ore at a constant temperature of 750 °C and a constant air rate of 49.5 cm/s, experiments were conducted with particle sizes classified in the intervals of 250-355, 355-500, 500-710 and 710-1000 μm and the results were graphed in Fig. 4. It is observed from the graph that calcination velocity is dependent on particle size and the decomposition rate increases with decreasing particle size, *i.e*., with increasing surface area. According to these data, it can be suggested that decomposition event takes place in the intermediate surface. In other words, it takes place according to the heterogeneous reaction model[11]. If the decomposition took place according to the homogeneous reaction model, than the particle size would be expected to be ineffective[12]. The maximum conversion reached is lower for particles

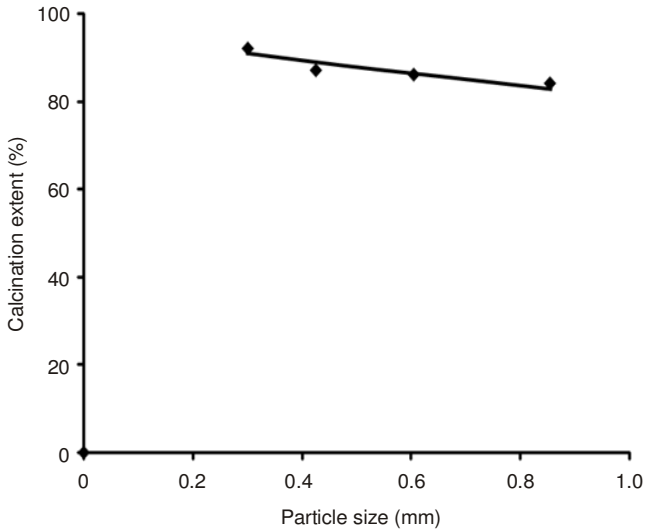

Fig. 4. Effect of various particle sizes on calcination at 750 °C and 49.5 cm/s flow rate

of bigger size. This finding can be attributed to the fact that product layer gets thicker in particles of bigger size and slows down the transfer events.

Effect of gas composition and temperature: In order to observe the effect of CO_2, which is a combustion byproduct present in furnace gases, experiments were conducted with samples of 355-500 μm particle size at two different temperatures (750 and 800 °C) and at 49.5 cm/s air flow rate containing CO_2 at various proportions and the calcination was examined in relation to time. The flow rate of CO_2 was arranged so that the air contained 0, 2, 4, 8 and 15 % CO_2. Fig. 5 displays the effect of CO_2 concentration on calcination at 750 and 800 °C. In Fig. 5, it is observed that increasing CO_2 rates decreased conversion rates at 750 °C. Although the calcination in mediums containing 0, 2 and 4 % CO_2 was high, the calcination in mediums containing 8 and 15 % CO_2 was very low. The trend observed at 800 °C appears to be significantly different from the trend observed at 750 °C. The difference observed in the conversion at 750 °C and the difference in decomposition in the medium containing 8 % or more CO_2 was not observed here.

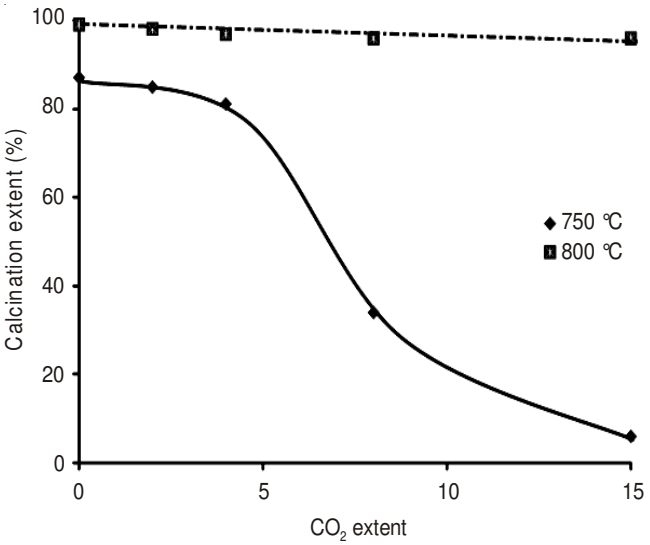

Fig. 5. Effect of CO_2 concentration on calcination at 750 and 800 C, 49.5 cm/s flow rate and 355-500 μm phosphate ore particle size

In order to explain this difference, experiments were conducted in mediums containing 8 % CO_2 at 700, 750, 800 and 850 °C and the results were plotted in Fig. 6. As can be seen in Fig. 6, the equilibrium pressure of calcite at 700 °C is lower than that of 8 % CO_2. Therefore, the calcination does not progress practically at 700 °C. However, increasing surface CO_2 pressure with increasing temperature is observed to emerge as the progressive power for the calcination. Significant differences are observed at 750 °C in terms of the amount of conversion and the conversion at 800 and 850 °C increased exorbitantly.

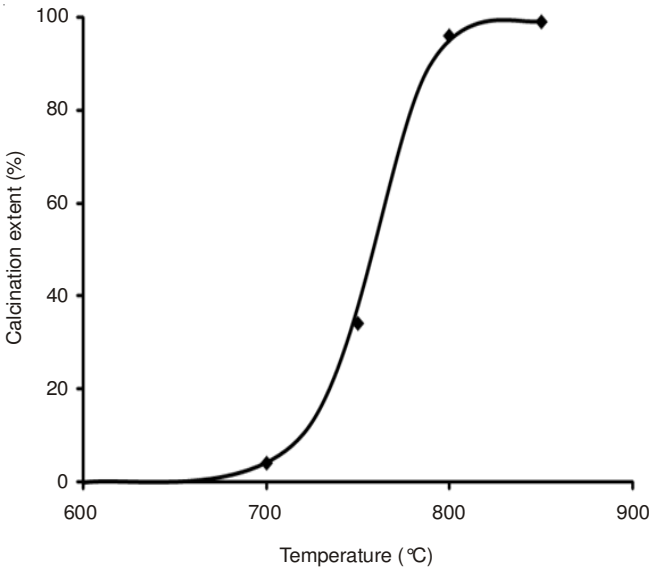

Fig. 6. Effect of temperature on calcination at 49.5 cm/s flow rate, 355-500 μm phosphate ore particle size and 8 % CO_2 concentration

In technological applications, calcination is performed in furnaces where direct heating is applied. In the furnace, the solid is in direct contact with the gases resulting from combustion of fuels. Among these gases, which are the byproducts of the combustion, CO_2 directly affects the calcination event. That is because the decomposition reaction of calcite is an equilibrium reaction and CO_2 is released as a gaseous by product of the reaction. The decomposition reaction is expressed as follows:

$$CaCO_3 \rightleftharpoons CaO + CO_2 \quad (6)$$

According to this reaction, at each temperature, a certain CO_2 pressure should be present on the solid phase. When the progress of the calcination is examined at 750 °C in gaseous mediums containing CO_2 at various proportions; it was observed that the calcination did not practically progress in the medium containing 15 % CO_2. In other words, the reaction is in equilibrium under these conditions and therefore it does not progress. The reaction accelerates with decreasing CO_2 ratio. Accordingly, this finding shows that the progress of the reaction increases with increasing difference in CO_2 concentration between phases. This is clearly observed in the initial conversions. However, with the progress of the reaction, *i.e.*, with increasing conversion, the difference between the rates of calcination decreases.

The results of the experiments,which were conducted at 800 °C in mediums containing different concentrations of CO_2,

show that under almost all conditions, the reaction progresses at increasing velocities with decreasing CO_2 pressure at the beginning. Under these conditions, a calcination reaction progressing very slowly did not emerge. That is because the equilibrium CO_2 pressure at 800 °C is much higher than the pressure of CO_2 in the air containing[4,6] 15 % CO_2. When the results are analyzed, the fact that conversions are equal in almost all CO_2 pressures shows that the reaction encountered the same resistance. This result can be explained by the presence of a solid product layer. Since the outflow of CO_2 becomes difficult beyond a certain product layer thickness and since the equilibrium pressure of CO_2 is the same for all samples under these conditions and also due to the fact that this external pressure is not effective inside this thick layer, similar conversions were obtained in all samples.

Modeling of the reaction: Thermal decomposition reaction of calcite is given in eqn. 6. In this study, the size of the solid did not change as a result of calcination. The porosity of the solid obtained at the end of the reaction increased[4,13]. In addition, it was also observed in this study that decreasing particle size increased the conversion rate (Fig. 4). All these findings suggest that calcination progresses according to the unreacted core model[11]. In this model, the solid forms a solid product layer as the reaction advances and therefore, a shrinking unreacted core is mentioned to exist inside. The solid product layer is generally referred to as the ash film. A series of steps given below can be considered to take place in the given order in the calcination reaction:

1. Heat transfer through the gas film
2. Heat transfer through the ash film
3. Formation of CO_2 in the interface between $CaCO_3$ and CaO
4. Reverse diffusion of CO_2 through the porous ash film
5. Diffusion of CO_2 through the gas film to the main gaseous medium.

It is assumed that the slowest progressing step among these controls the reaction velocity[11]. According to the unreacted core model where the ash film is formed, the conversion-time relations for the heat or mass transfer control from fluid film, the chemical reaction control on the unreacted core surface and the diffusion control from ash film are described with the following relations, respectively[11-15].

$$kt = X \quad (7)$$

$$kt = 1-(1- X)^{1/3} \quad (8)$$

$$kt = 1-3(1-X)^{2/3} + 2(1-X) \quad (9)$$

In these relations, k, t and X represent the apparent velocity constant, the reaction time and the conversion fraction, respectively.

The results obtained on the 15th min where the reaction reached its steady state were used in the experiments investigating the effect of temperature on calcination. The conversion rates here were substituted in eqns. 7-9 and their graph was drawn according to the Arrhenius expression (Fig. 7).

$$k = A \cdot e^{-Ea/RT} \quad (10)$$

Arrhenius constant A and the activation energy E_a were calculated according to the Arrhenius expression[16] shown in (10).

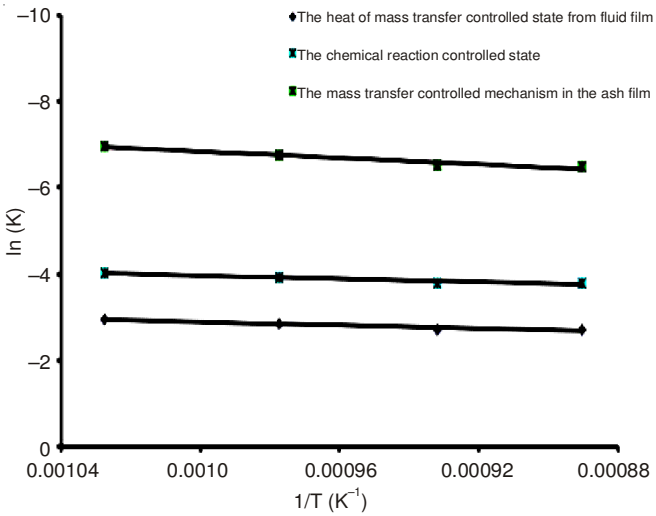

Fig. 7. Arrhenius plots of reaction rates for calcination of phosphate rock

Using this graph of the Arrhenius relationship, the following results were calculated for the heat or mass transfer controlled state from fluid film:

$$A = 0.353 \text{ min}^{-1} \quad E_a = 15.33 \text{ kJ/mol}$$

for the chemical reaction controlled state:

$$A = 0.125 \text{ min}^{-1} \quad E_a = 15.65 \text{ kJ/mol}$$

and for the mass transfer controlled mechanism in the ash film:

$$A = 0.045 \text{ min}^{-1} \quad E_a = 31.08 \text{ kJ/mol}$$

The fact that the activation energies calculated for the heat or mass transfer controlled mechanism from fluid film and chemical reaction controlled mechanism are smaller validates these mechanisms. The compatibility of the activation energy calculated for the ash film mass transfer controlled mechanism confirms this mechanism.

Conclusion

Using the data obtained in this study, it was concluded that the calcination of Mazidagi phosphate rock was compatible with the unreacted core model among the heterogeneous reaction models. Both the fact that particle size is much more effective and the results of the Arrhenius equality support the transfer mechanism from ash film. The reason for the decrease in yield with increasing particle size can be explained by the fact that the layer forming on the surface of the solid gets sintered at high temperatures and affects the gas output rate. In addition, the fact that the flow rate of the gas is very much effective suggests that controlled transfer mechanism from fluid film affects the calcination as well. However, it can be proposed that the step determining the velocity of the calcination reaction is the mass transfer controlled mechanism of CO_2 in the ash film with 31.08 kJ/mol activation energy.

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