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The chlorination kinetics of zirconium dioxide mixed with carbon black

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ABSTRACT

In this research, the effects of chlorine gas at different chlorine partial pressures and carbon concentrations on the carbochlorination of zirconia were studied. It was found that in briquettes containing 18.7 %wt carbon, in a chlorine partial pressure range of 0.25–0.75 atm and for a reacted fraction of less than 0.7, the chemical reaction model was dominant for the carbochlorination process of zirconia. The order of reaction into chlorine gas (n) in this situation was 0.57. Moreover, the best weight ratio of carbon to zirconia was 40/60. In this case, the activation energy of the reaction was 209.9 kJ mol^{-1} in a temperature range of 1023–1223 K, and the dominant model was the chemical reaction model.

1. Introduction

High purity ZrO_2 (>99 %wt) is used for coating TiO_2 pigments. This material can be substituted for TiO_2 pigment in preparing white and special colors. Pure zirconia is used as a solid electrolyte in oxygen sensors and fuel cells. Optical fibers can also be produced by ZrO_2. The zirconia–lead–titanium piezoelectric (PZT) is utilized in microphone crystals, phonographs and medicine ultrasonic photography. Transparent and active optical ceramics (PLZT) can be prepared by the addition of small amounts of lanthanum to these piezoelectrics. Moreover, cubic single crystals of zirconia have many applications in gem industries [1,2].

One of the most suitable methods to produce high purity zirconia is the chlorination of impure zirconia in the presence of carbon. Sublimation and partial solidification processes in a temperature range of 623–673 K are used to remove impurities from the $ZrCl_4$. The reaction between purified solid $ZrCl_4$ and water steam produces high purity ZrO_2. Chlorination in the presence of carbon is also an important step in the large scale, commercial production of titanium and zirconium [1,3,4].

Chlorine and ZrO_2 in a temperature range of 1000–1100 K do not react thermodynamically, and completion of this reaction requires a reducing agent such as carbon. Thus, the reaction is called carbochlorination [5,6].

Carbochlorination is a reaction through which metallic chloride is obtained in the presence of a carbonaceous material in dry conditions [7]. Presence of carbon reduces the propensity of oxide formation and favors the formation of chlorides by providing a low oxygen potential atmosphere [8,9]. The rate of the reaction of carbochlorination is faster than the chlorination reaction at the same high temperature [10]. The necessity of a reducing agent can be understood by calculating the free energy changes of the reactions shown in Table 1 (Eqs. (1)–(6)), which can take place during ZrO_2 chlorination [5]. The proposed mechanism of the carbochlorination reactions comprises the following stages: 1 – formation of chlorine atoms on the carbon surface; 2 – chlorination of refractory oxides with chlorine atoms; and 3 – carbon oxidation [11,12].

According to data shown in Table 1, reaction 1 cannot occurs at 1100 K while other reactions can occur over this temperature range, thermodynamically. Reaction 3 could simply be the overall result of reactions 2 and 5 [5]. Various researchers have found that the CO fraction in the gas mixture during the carbochlorination process increases with temperature. It has been found that reaction 5 ($CO_2 + C = 2CO$) is slower than the chlorination reaction of ZrO_2 in the presence of carbon at 1075 and 1275 K [5,13].

O'reilly and Doig [5] found that in the carbochlorination of ZrO_2 in the temperature range of 1223–1373 K the chemical reaction model controls the process and the activation energy and order of reaction into Cl_2 are 230.3 kJ mol^{-1} and 0.64, respectively. The kinetics and various parameters of the carbochlorination of ZrO_2 have also been reported by others [14]. They have claimed that the

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Table 1
Carbochlorination reactions of ziconia and their Gibbs free energy change (5).

Reaction		Temperature (K)	ΔG (kJ mol^{-1})
$ZrO_2 + 2Cl_2 = ZrCl_4 + O_2$	(7)	1000	154.2
		1100	147.1
$ZrO_2 + C + 2Cl_2 = ZrCl_4 + CO_2$	(8)	1000	−241.2
		1100	−248.3
$ZrO_2 + 2C + 2Cl_2 = ZrCl_4 + 2CO$	(9)	1000	−245.7
		1100	−270.4
$ZrO_2 + 2CO + 2Cl_2 = ZrCl_4 + 2CO_2$	(10)	1000	−236.6
		1100	−226.6
$CO_2 + C = 2CO$	(11)	1000	−4.6
		1100	−22.0

dependence of the chlorination rate on the chlorine partial pressure up to 0.7 atm is linear.

Bicerolu and Gauvin [13] have studied the effect of the carbon concentration on the carbochlorination process of ZrO_2 in the temperature range of 1400–1950 K and have found that the maximum rate of process can be achieved in the carbon concentration range of 22–26 %wt. Moreover, they have reported 94 kJ mol^{-1} and 0.79 as the activation energy and order of reaction into Cl_2, respectively.

In this research, the effects of the chlorine partial pressure and the carbon concentration on the reaction rate of the carbochlorination process of ZrO_2 briquettes in a thermogravimetric analysis (TGA) apparatus, using inert gas, were studied.

2. Raw materials and procedure

The chemical compositions of ZrO_2 (size of 80% of the particles according to ASTM 4188 was in the range of 70–140 μm), carbon black (size of 80% of the particles according to ASTM 4188 was in the range of 45–70 μm) used in this research and ash composition are shown in Table 2. The Cl_2 and Ar gases with purities of 99.80 %wt and 99 %wt were used in all the experiments.

The mixture of 18.7–70 %wt carbon black and ZrO_2 were used to prepare briquettes with a weight of 32 ± 0.1 g, a volume of 16 ± 0.1 cm^3, and a porosity of 20–25% by pressing. The briquettes were dried at 413 K in a tray drier [15]. A schematic of the designed thermogravimetric analyzer apparatus used in this research is shown in Fig. 1. In this analyzer, a briquette is laid in the quartz sample holder contacted to a suitable (Pt: Pt–10 %Rh) thermocouple to measure the temperature. A sample of Al_2O_3 (purity 99.9 %wt) with volume similar to briquettes was used for system calibration. Information about the analyzer and calibration experiments has been reported elsewhere [16].

On the basis of other reports that showed the effect of gas flow rate on the carbochlorination process, the gas flow rate was fixed at 400 l h^{-1} in all the experiments to avoid the effects of gas flow rate on results [17].

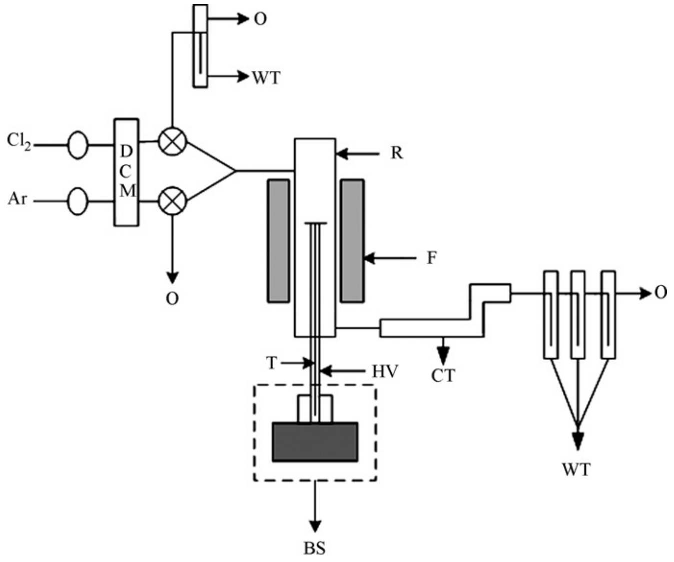

Fig. 1. Schematic of the thermogravimetric analyzer used in this research. DCM, device for the drying, control and measurement of the gases; O, outlet; WT, washing traps; R, reactor; T, thermocouple; HV, quartz holding vessel; F, furnace; BS, weighting system; CT, collecting tube.

The briquettes with various fractions reacted in Ar–Cl_2 atmosphere after weighting were exposed to air at 1400 K to remove the carbon content of the residue. Then the residues were analyzed with X-ray fluorescence (XRF) to define the amount of zirconia and other refractory oxides in the remaining samples. The difference between the amount of initial and final contents of ZrO_2 in the samples determined the amount of chlorinated ZrO_2. According to the results of this experiment, the weight changes of zirconia were calculated from total weight decrease in chlorinated briquettes according to Eq. (6):

$$\Delta m_{(ZrO_2)} = (0.84 \pm 0.02)\Delta m_t \qquad (1)$$

where Δm_t and $\Delta m_{(ZrO_2)}$ are the total weight decrease and weight changes of zirconia in the samples, respectively. Other researchers used a similar equation to calculate the amount of chlorinated zirconia [13,18].

3. Results and discussion

3.1. Effect of chlorine partial pressure

Fig. 2 shows the effect of chlorine partial pressure on the chlorination process of samples containing 18.7 %wt carbon at 1223 K and a gas flow rate of400 l h^{-1}. Experiments have been performed in chlorine partial pressures of 0.25, 0.33, 0.50, 0.66, and 0.75 atm and a total pressure (Cl_2 plus Ar) of 1 atm. The reacted fraction (*X*

Table 2
Analysis of raw materials and ash.

Zirconia		Carbon black		Composition of ash in briquette containing 50% carbon and reacted fraction of 0.8	
Composition	wt%	Composition	wt%	Composition	wt%
HfO_2	1.6	Al	0.3	C	78.53
MgO	0.6	Fe	1.1	ZrO_2	19.13
Fe_2O_3	0.05	Si	0.5	HfO_2	0.31
SiO_2	0.8	Cu	0.65	SiO_2	2.03
Al_2O_3	0.8	Na	0.01		
As_2O_3	0.2	Ni	0.02		
ZrO_2	95.95	Ba	0.01		
		Volatiles	2.5		
		Fix C	93.21		

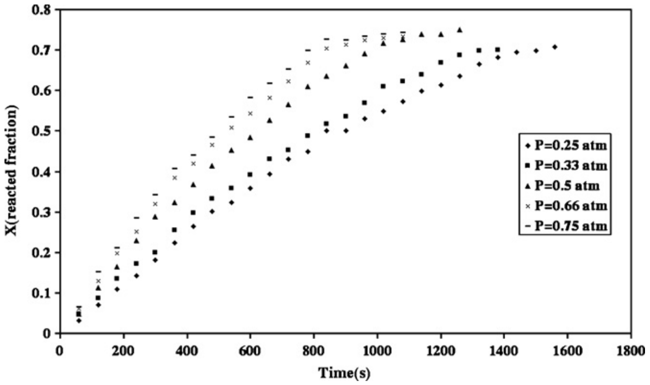

Fig. 2. Changes of the reacted fraction versus time at various chlorine partial pressures at a temperature of 1223 K and a gas flow rate of 400 l h^{-1} (samples contain 18.7 %wt carbon).

(has been calculated from Eq. (7):

$$X = \frac{\Delta m_{(ZrO_2)}}{m_0} \tag{2}$$

where m_0 is the primary weight of ZrO_2 in the briquette, and $\Delta m_{(ZrO_2)}$ is calculated from Eq. (6).

It is seen from Fig. 2 that increasing the chlorine partial pressure leads to the improvement of the reacted fraction at a constant time in the carbochlorination process.

3.1.1. The overall rate equation

Kinetics models based on Eq. (8) [19] were used to study the kinetics of carbochlorination reactions.

$$g(X) = kt \tag{3}$$

where $g(X)$, t and k are the description function of the reaction mechanism versus X (reacted fraction), reacting time and rate constant, respectively.

Fig. 3 shows the chemical reaction model [19] (Eq. (9)) versus t, calculated from the results depicted in Fig. 2 at various chlorine partial pressures.

$$g(X) = 1-(1-X)^{(1/3)} \tag{4}$$

According to the linear status of graphs in Fig. 3 up to $g(x) = 0.35$, the chemical reaction mechanism is dominant in these experiments. The slope of each linear graph in Fig. 3 represents the rate constant of reaction in the corresponding condition. Fig. 3 also shows that above $X = 0.725$ or $g(X) = 0.35$, this model is not valid at all chlorine partial pressures.

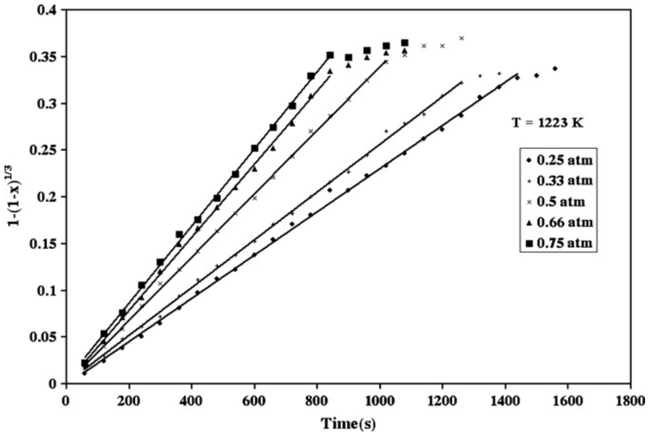

Fig. 3. Changes of $1-(1-X)^{(1/3)}$ versus reacting time at various chlorine partial pressures at 1223 K and a gas flow rate of 400 l h^{-1} (samples contain 18.7 %wt carbon).

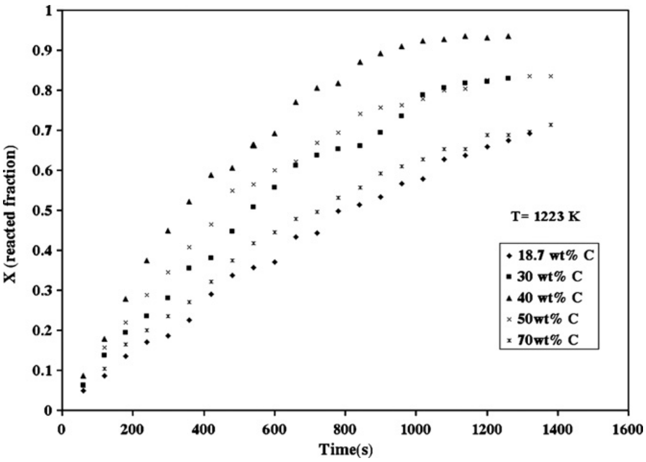

Fig. 4. Changes of reacted fraction versus reacting time at1223 K, a gas flow rate of 400 l h^{-1} and a chlorine partial pressure of 0.3 atm.

Wen [20] extended the Yagi and Aochi model [21] for heterogeneous gas/solid reactions controlled by a chemical reaction mechanism and obtained the rate constant k in Eq. (10) [19].

$$k = AT^q \exp -\left(\frac{E}{RT}\right) p_{Cl_2}^n \tag{5}$$

where n, E, A, q, and T are the order of carbochlorination reaction, activation energy, exponential preliminary factor consisting of the diameter and density effects of particles, constant number and temperature in Kelvin, respectively.The order of carbochlorination reaction can be calculated from Eq. (10), and the k values can be obtained from the slopes of lines in Fig. 3. Dependence of ln(10,000 k) on ln(10 P_{Cl_2}) shows good linearity with the correlation coefficient (R^2) of 0.9891. Accordingly the order of carbochlorination reaction is 0.57.

Wen [20] stated that the order of reaction with respect to the gaseous reactant may vary from 0 to 2 depending on the ease of adsorption of the reactant gas on the surface of the solid. According to O'reilly and Doig [5], a fractional order of 0.6 indicates the dissociation of the Cl_2 molecule on the surface of the oxide. The order of reaction obtained in this research implies that a similar phenomenon occurred in the condition of these tests.

3.2. Effect of carbon on the carbochlorination process

Fig. 4 shows the effect of carbon concentration on reacted fraction at a temperature of 1223 K, a gas flow of 400 l h^{-1} and a chlorine partial pressure of 0.3 atm. Samples containing 70, 50, 40, 30 and 18.7 %wt carbon were used in these studies.

According to Fig. 4, increasing the carbon content up to 40 %wt of the briquettes leads to an increase in the chlorination rate and X value at constant time. After this amount, the reaction rate and X value decrease. Therefore, it seems that 40 %wt carbon in the briquettes is the optimum amount for the carbochlorination process.

Various models have been examined on the basis of Eq. (8) to determine the kinetic model in various carbon content briquettes. It has been found that the chemical reaction model (Eq. (9)) is valid for carbon contents lower than 40 %wt (Fig. 5). On the basis of other studies in briquettes containing 18.7 %wt carbon, the chemical reaction model with an activation energy of 250.8 kJ mol^{-1} in a temperature range of 1023–1223 K and a chlorine partial pressure of 0.3 atm is dominant [17]. Fig. 5 shows that at 1223 K this model is valid as a good approximation in the samples containing 30 %wt carbon in the range of $g(X) \leq 0.43$ ($X \leq 0.81$). The briquettes contain-

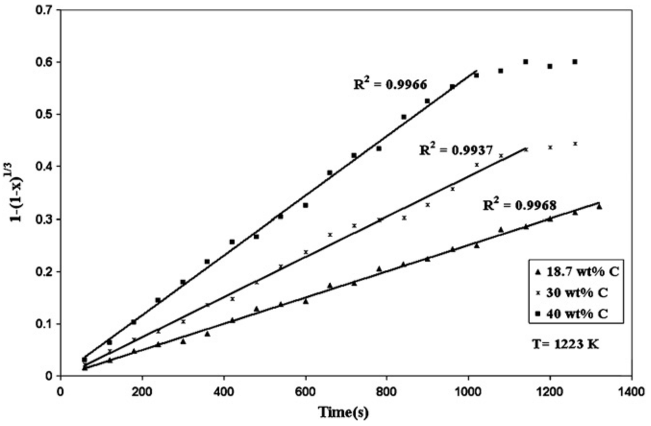

Fig. 5. Changes of $g(X) = 1 - (1-X)^{(1/3)}$ versus reacting time at 1223 K, a gas flow rate of 400 l h^{-1}, and a chlorine partial pressure of 0.3 atm for samples containing 18.7, 30 and 40 %wt carbon.

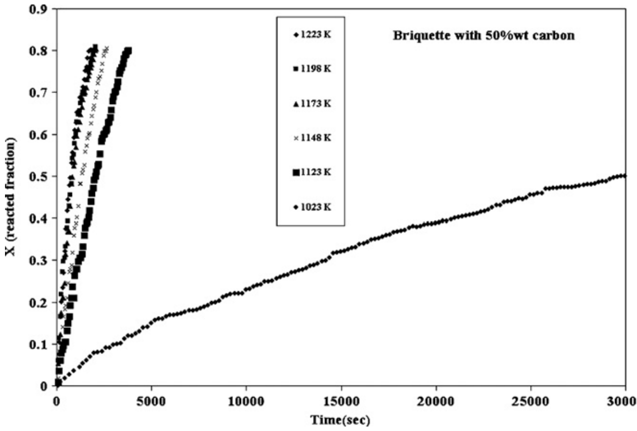

Fig. 6. Changes of reacted fraction versus time at various temperatures for briquette containing 50 %wt carbon.

ing 40 %wt carbon also obey this model in the range of $g(X) \leq 0.57$ ($X \leq 0.92$). The slope of the lines in Fig. 5 determines the reaction constant (k). Fig. 6 shows the plot of X versus time for briquettes containing 50% carbon in the temperature range of 1023–1223 K. Fig. 7 shows that Eq. (11) (pore diffusion model) shows the best agreement with experimental results for the briquettes with more than 40 %wt carbon.

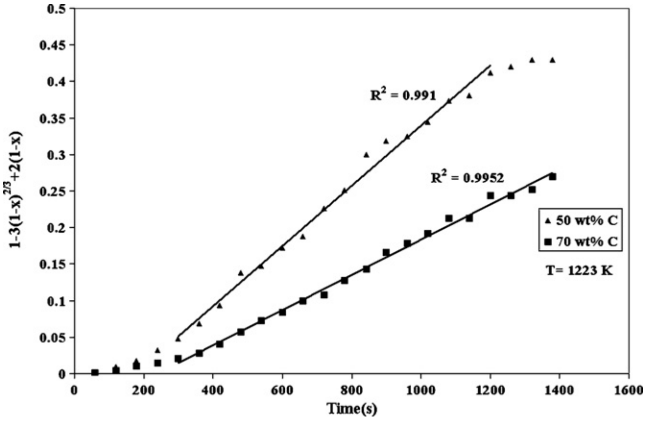

Fig. 7. Changes of $g(X) = 1 - 3(1-X)^{(2/3)} + 2(1-X)$ versus reacting time at 1223 K, a gas flow rate of 400 l h^{-1}, and a chlorine partial pressure of 0.3 atm for samples containing 50 and 70 %wt carbon.

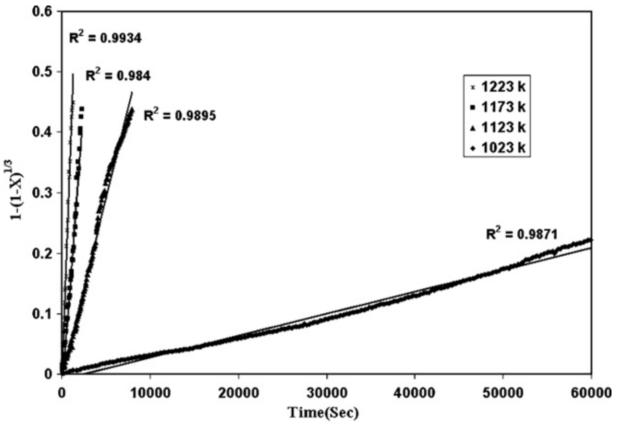

Fig. 8. Changes of $g(X) = 1 - 3(1-X)^{(1/3)}$ versus reacting time at 1223, 1173, 1123 and 1023 K, a gas flow rate of 400 l h^{-1}, and a chlorine partial pressure of 0.3 atm for samples containing 30 %wt carbon.

$$g(X) = 1 - 3\,(1-X)^{(2/3)} + 2(1-X) \tag{6}$$

Eq. (11) is dominant when the reaction is controlled by the diffusion of reactants and gaseous products across the solid layer (ash). This equation applies for pore diffusion control in the reaction of porous or nonporous solids with a porous product layer [19].

At 1223 K in briquettes containing 50 %wt carbon in the range of $0.02 \leq g(X) \leq 0.42$ ($0.24 \leq X \leq 0.83$) the curves are linear (Fig. 7). Linearity is valid in briquettes containing 70 %wt carbon in the range of $0.013 \leq g(X) \leq 0.28$ ($0.19 \leq X \leq 0.72$).

In briquettes containing less than 40 %wt carbon, the chemical reaction is dominant, and diffusion of Cl_2, $ZrCl_4$ or CO across the ash layer controls the kinetic of process above 40 %wt.

The product of the carbochlorination process of zirconia is not solid. It seems that excess carbon in samples containing 50 and 70 %wt carbon creates a porous surface (including the non-reacted carbon), and then diffusion of chlorine gas through this surface into the briquette or diffusion of CO and $ZrCl_4$ gas through this surface out of the briquette (the slowest step of the reaction) controls the process. Therefore, we conclude that with carbon content increasing from 18.7 %wt to 40 %wt the reaction rate improves due to the increase of carbon in Eq. (3) and/or due to the quasi-catalytic effect of carbon in the carbochlorination process [12–14]. At a temperature of 1223 K, if the carbon content increases to amounts higher than 40 %wt, the diffusion of gases into or out of the briquettes is slower than the chemical reaction.

Various models based on Eq. (8) were applied to study the kinetics of samples containing 30 %wt carbon at temperatures of 1023, 1123, 1173, and 1223 K. Fig. 8 shows that in these samples Eq. (9) (the chemical reaction model) versus time is linear. Therefore, the chemical reaction model is dominant, and the rate of reaction is controlled by the chemical reaction in the temperature range studied.

The slope of the $1 - (1-X)^{(1/3)}$ curve versus time in Fig. 8 is equal to k (the reaction rate constant). According to Eq. (10) dependence of ln k versus 10,000/T shows good linearity with the correlation coefficient (R^2) of 0.9903. The slope of this line is equal to $-E/R$ in which E and R stand for the activation energy and the gas constant, respectively (for simplicity of calculation, it is assumed that $q = 0$ [5]). Accordingly, the activation energy of the process was calculated at 234.8 kJ mol^{-1} for the briquettes containing 30 %wt carbon. It has been reported that the activation energy of the carbochlorination reaction of ZrO_2 is 250.8 kJ mol^{-1} for samples containing 18.7 %wt in the temperature range of 1023–1223 K [17].

Table 3
Activation energy of cabochlorination reaction for briquettes containing various amounts of carbon.

Carbon wt%	Temperature range (K)	Activation energy (kJ mol^{-1})	Carbochlorination mechanism
18.7	1023–1223	250.8	Chemical reaction
30	1023–1223	234.8	Chemical reaction
40	1023–1223	205.9	Chemical reaction
50	1023–1173	220.1	Chemical reaction
	1198–1223	69.6	Pore diffusion
70	1023–1148	192.1	Chemical reaction
	1173–1223	73.6	Pore diffusion

The activation energies of other briquettes with different carbon content were calculated in a temperature range of 1023–1223 K and listed in Table 3. According to this table, the value of the activation energies for samples containing 50 %wt and 70 %wt carbon are different from other samples in the temperature ranges of 1198–1223 and 1173–1223 K, respectively. These values demonstrate that in these temperature ranges the kinetics model changed.

4. Conclusions

According to the results of the present research, the following conclusions were drawn.

1. The chemical reaction model at 1223 K was dominant for the carbochlorination process of zirconia in the case of briquettes containing 18.7 %wt carbon and a reacted fraction $(X) \leq 0.7$ in the pressure range of 0.25–0.75 atm.
2. The reacted fraction and the rate of the carbochlorination process improved with the increasing chlorine partial pressure. The order of carbochlorination reaction (n) was equal to 0.57 for samples containing 18.7 %wt carbon.
3. Increasing the carbon content from 18.7 to 40 %wt led to an increase in the reaction rate at 1223 K.
4. Increasing the carbon amount in the samples containing more than 40 %wt carbon led to a decrease in the reaction rate at 1223 K.
5. In the briquettes containing 18.7, 30 and 40 %wt carbon, the chemical reaction model in the temperature range of 1023–1223 K was dominant.
6. The chemical reaction model was dominant in samples containing 50 %wt and 70 %wt carbon in the temperature ranges of 1023–1173 and 1023–1148 K, respectively. But in the temperature ranges of 1198–1223 and 1173–1223 K the carbochlorination reaction was controlled by the pore diffusion.
7. When the chemical reaction model was dominant (except for samples containing 50 %wt carbon), the activation energy decreased with increasing carbon content.

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