The kinetic model for carboreduction of zinc oxide

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Abstract. The carbothermal reduction of zinc oxide using highly concentrated solar radiation is a promising concept for the production of pure zinc and hydrogen. Solar energy is converted to chemical energy in the form of abundant fuel, easy to use and environmentally friendly. The present work is aimed to study kinetics of carboreduction of zinc oxide in laboratory reactor, developing the kinetic model and explore the possibility to accelerate the process (decrease in CO_2 concentration) by adding a catalyst to the solid ZnO and carbon mixture. A laboratory experimental set up for kinetic study of carbothermal reduction of zinc oxide is constructed and described in details. Experiments were carried out with mixtures of zinc oxide powder and 12-20 mesh activated carbon at temperatures of 1000-1300 °C and C/ZnO wt. ratios =1:8. A kinetic model was proposed based on a mechanism of carboreduction that involves two chain gas-solid reactions with intermediate formation of CO and CO_2. The rate constants and activation energy were determined from the experimental data. The validity of the model is discussed. The preliminary experiments were carried out on catalytic carboreduction of Zinc Oxide. The sample for catalytic carboreduction was prepared by impregnation of the ZnO + C mixture with Nickel acetate solution. Two samples containing ZnO + C mixture and ZnO + C + 2%NiO were tested at 1000 °C under the same conditions. It was found that adding Ni-catalyst to the mixture of Graphite and ZnO increases drastically the rate of carboreduction and conversion of Zinc Oxide.

1. INTRODUCTION

Solar thermochemical endothermic processes make use of concentrated solar energy as the source of the high temperature process heat. The reduction of metal oxides is an example of such processes. The products are the metals which can be used for generating hydrogen via hydrolysis. The product of hydrolysis is the metal oxide which is recycled to the solar reactor. The cycle with ZnO is very attractive for conversion , storage and transportation of solar energy since: the solar contribution is high (about 60 %) ; CO, and H_2 can be in situ separated and the amount of energy that can be recovered is up to 2.6 times the electric energy that can be gained by conventional combustion of carbon input.

Murray, Steinfeld and Fletcher [1] have examined the thermodynamics of the carbothermal reduction of metal oxides in either nitrogen or argon atmospheres. Zinc oxide can be reduced with carbon at temperatures of 1000-1300 °C without formation of carbides or low-valence oxides. The reaction, which is the first step of a two-step thermochemical scheme, can be presented as:

$$ZnO + C = Zn + CO \qquad (1)$$

In the second step, the metal is further reacted with water to form molecular hydrogen according to:

$$Zn + H_2O = ZnO + H_2 \qquad (2)$$

The first step is quite common in metallurgy. Zinc pyrometallurgy is based upon reduction of zinc oxide with CO:

$$ZnO\,(S) + CO\,(G) \Leftrightarrow Zn\,(G) + CO_2\,(G) \qquad -47.8\ \text{kcal/mole} \qquad (3)$$

$$CO_2\,(G) + C\,(S) \Leftrightarrow 2\,CO\,(G) \qquad -34.9\ \text{kcal/mole} \qquad (4)$$

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Both reactions are reversible and the overall reaction is endothermic. Difficulties arise because (a) zinc has low boiling point (907 °C), (b) a high temperature is required for reduction of zinc oxide with carbon, and as a result, liquid zinc cannot be obtained in a shaft furnace, and (c) the principal reduction reaction (3) tends to reverse at low temperatures and the condensation of zinc is difficult.

There is a fundamental difference between the solar and the conventional carbothermal reduction of solid zinc oxide. In the conventional process such as the Imperial Smelting Furnace [2], the reducing agent is burnt to supply the reaction heat. This results in higher quantities of CO_2, which cause back reaction. The gas that finally leaves the furnace has the approximate composition of 7.5-8.8 % (mole) Zn vapor, 7.5-14 % CO_2 and 16-25% CO, the remainder being nitrogen [2]. In the solar process, if carbon is used as the reducing agent, CO is the main gaseous compound with only a small amount of CO_2. The equilibrium CO_2/CO ratio at temperatures of 1100-1300 °C is only about 10^{-3}-10^{-4}. If the condenser operates at 550 °C, the CO_2/CO ratio should be below $3.2*10^{-4}$ to avoid oxide formation. The CO_2 concentration could be kinetically controlled. If coal is used as a reducing agent, H_2O should also be in the products. This results in increasing the rate of back reactions. Therefore, the kinetics of carboreduction and back reactions must be investigated experimentally for developing new solar technology.

Reduction of ZnO was studied in a solar receiver [1]. Three runs were performed 1) at 1550 K for 30min., 2) 2040 K for 5 min. and 3) 2080 K and 0.1 ATM for 15 min. The yield, defined as the amount of zinc produced versus the theoretical amount that would have been recovered if the reaction goes to completion, was 13, 42 and 62% respectively. Kinetics of gasification of coal with ZnO was studied by Tsuji et. al. [3]. It was shown that conversion of coal to CO increased with an increasing ZnO/carbon molar ratio. In this paper the kinetics of thermal reduction of zinc oxide is presented and the kinetic model is proposed. Preliminary results on catalytic carboreduction of zinc oxide are discussed.

2. EXPERIMENTAL

The experimental set up for kinetic study of carbothermal reduction of zinc oxide is presented in Fig 1. The main parts of the set up are: two furnaces with temperature control , reactor-sampler for pretreatment at 500-600 °C, reactor for high temperature operation, flow meters, vacuum system, analytical unit with GC, data logger and PC for data collection and recording. The sample after pretreatment can be moved to the high temperature reactor.

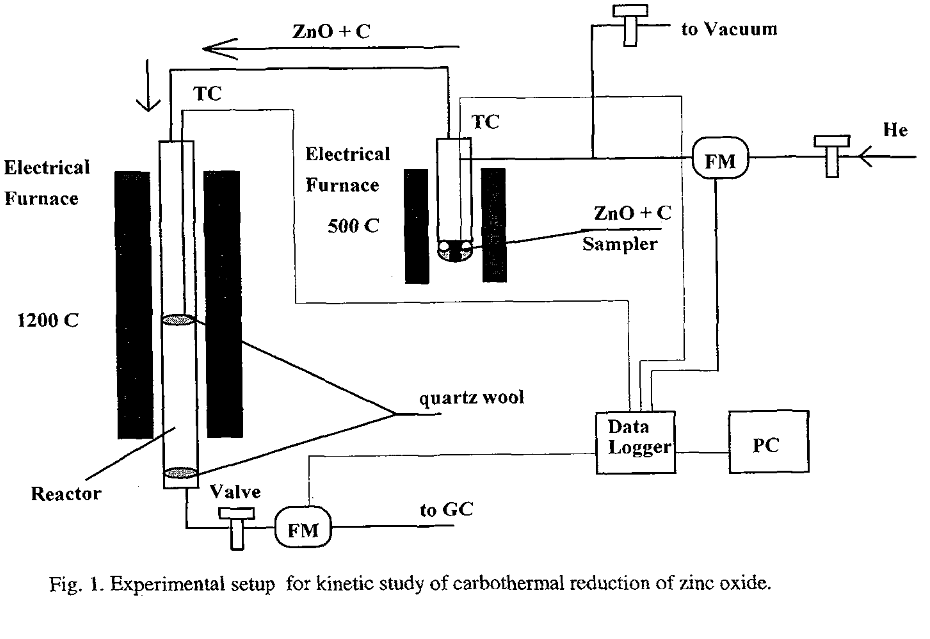

Fig. 1. Experimental setup for kinetic study of carbothermal reduction of zinc oxide.

Pellets (discs) were prepared for kinetic studies from Graphite and ZnO powder mixtures with C/ZnO ratio=1. The sizes of the pellets were 10 * 2mm and 20*5mm. The pellets were prepared by a press and forms used originally for IR spectroscopy. Fractures of 5-7 mm were also prepared from the large pellets.

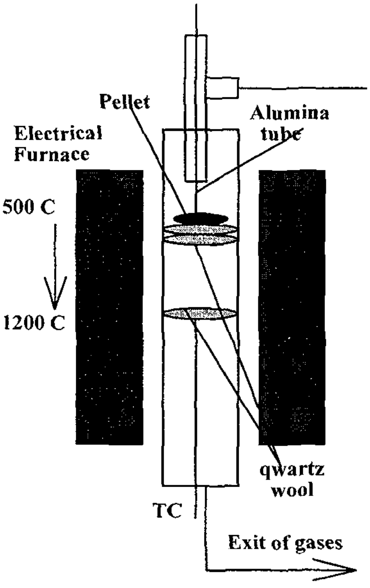

Fig.2. Reactor for study kinetics of carboreduction of ZnO with pellets.

The reactor is shown in Fig 2. The sample after pretreatment can be moved down from low to the high temperature zone in the reactor by alumina tube.

The following materials were used:

Graphite powder synthetic, from BHD Chemical Ltd., England. Activated carbon, Darco,12-20 mesh, from Aldrich Chemical Company. Zinc oxide powder, from Merk, Germany. Zinc acetate dehydrate , from Fisher , USA.

Experiments were carried out with mixture of zinc oxide powder and activated carbon 1-2 mm, pellets prepared of graphite and ZnO powder mixtures at temperatures 1000-1300 °C. In experiments with activated carbon particles and ZnO powder the weight of zinc oxide sample was 1-2 gr, weight of activated carbon was 2gr. Flow rate of inert gas (Helium) was 40 cc/min. Preliminary experiments were conducted by heating of a mixture of ZnO powder with activated carbon under Helium flow up to 600 °C. CO and CO_2 were detected in the gas phase by GC. Liquid water was collected in a trap. The water quantity was about 15% wt. of the initial weight of carbon particles. Therefore, all the kinetic experiments were carried out after calcination of the reaction mixture at 500 °C for 1hr under vacuum.

3. RESULTS

Fig.3 shows the results obtained at 1200 °C with ZnO powder and activated carbon of different sizes of the particles (1-2 and 2-6 mm). The size of particles effected drastically the rate of reaction.

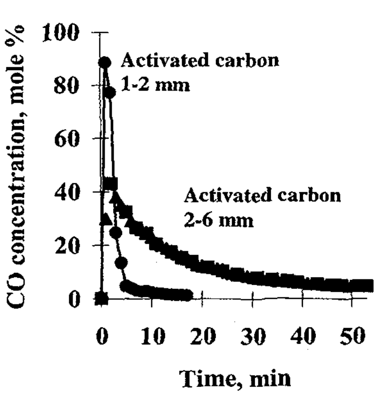

Fig 3. Plot of the CO concentration versus time. ZnO powder (2gr) , activated carbon 2-6 and 1-2 mm. C/ZnO ratio =1 (wt.). Temperature 1200 °C .

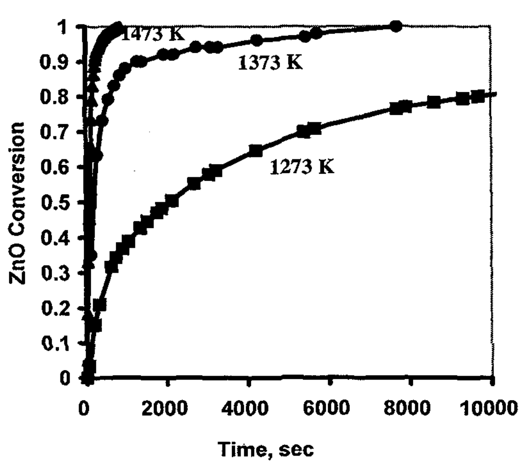

Fig 4. Plots of ZnO conversion versus time at different temperatures. ZnO powder and activated carbon 1-2 mm (2gr).

In the case of 1-2 mm carbon particles, a conversion of about 90% can be obtained within reaction time of 10 min. In the experiment with 2-6 mm carbon particles a conversion of about 50% was obtained after one hour. Experiments were carried out at temperatures of 1000-1300 °C with mixture of zinc oxide powder and 1-2 mm activated carbon. The weight of zinc oxide sample was 1-2 gr, weight of activated carbon was 2gr. The results obtained at temperatures 1000-1200 °C are given in Fig. 4. It can be seen that rate of reaction at temperature of 1000 °C is low; about 4 hours are needed to reach the ZnO conversion of 86%. At 1100 °C the time of reaction is reduced down to 15-20 min, and at 1200 °C the reaction is completed in 10 min.

The experiments show that at temperatures 1000-1200 °C the CO_2 concentrations are much higher than the equilibrium values. At temperatures of 1000-1100 °C the maximum CO_2 concentrations were found to be 0.75 and 0.25 % respectively. Special experiments were carried out to find conditions for operation at 1200 °C with minimum CO_2 concentrations. The CO_2 can be partly removed by additional gasification of carbon under isothermal conditions. The mixture of ZnO powder (1-2 gr) and activated carbon (2 gr) was placed in the sampler. Activated carbon (4-16gr) was placed also in reactor. This part of the carbon was calcinated at 1200 °C under He flow for 2 hours. The results of this experiments shows that excess of carbon as high as 8-10 (wt) is needed to reduce the CO_2 concentrations close to the equilibrium values. At temperature of 1300 °C the CO_2 concentration was lower than the sensitivity of thermal conductivity detector (10^{-2} mole %).

Experiments were carried out also with pellets having 10mm diameter and 2mm height (prepared from zinc oxide powder and graphite mixture) and fractures of 5-14mm and 5-7 mm at temperatures of 1000-1200 °C. Weight of the samples was 1.8-2.2 gr. It was found that at 1200 °C the reaction is practically completed 10-12 min after its initiation, even in the case of large pellets. The maximum CO_2 concentration was 0.5-0.7%. Pellets of 3-4 mm are recommended for the solar reactor for operation at 1200-1300 °C.

4. CATALYTIC CARBOREDUCTION OF ZINC OXIDE

It is assumed that the mechanism of carboreduction of ZnO comprises the chain reactions (3) and (4) with intermediate formation of CO and CO_2. The first reaction is reduction of ZnO with CO and the second one is gasification of carbon with CO_2. The catalytic gasification of coal is a well known process [4]. If the mechanism of carboreduction of ZnO via reactions (3)-(4) is valid, the process should be catalyzed by coal gasification catalysts : K, Ca, Fe or Ni. Preliminary experiments were carried out on catalytic carboreduction of Zinc Oxide. Large pellets (discs) D=20mm, h=5mm were prepared of Graphite and ZnO powders mixture with C/ZnO ratio=1. The pellets were crushed to fractures with particle size 5-7 mm. The sample for catalytic carboreduction was prepared by impregnation of the ZnO + C mixture with Nickel acetate solution following by drying at 200 °C for 10 h and calcination at 350 °C for 5h. After this procedure the sample contents ZnO +C mixture and about 2% of NiO. Two samples containing ZnO + C mixture and ZnO + C + NiO were heated to 1000 °C under the

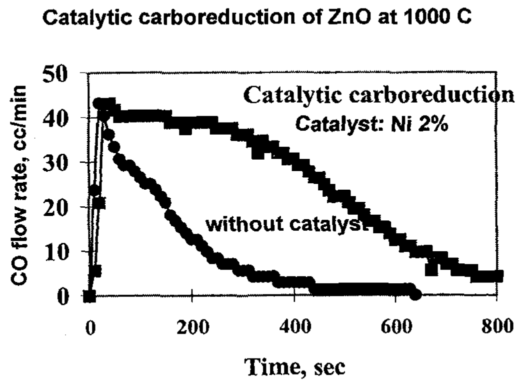

Fig. 5. Effect of Ni-catalyst on carboreduction of zinc oxide at 1000 °C. Mixture of ZnO + Graphite, wt. Ratio=1, particles 5-7 mm. Plots of the CO flow rates vs. time.

same conditions. The results are presented in Fig.5. It can be seen that adding Ni-catalyst to the mixture of Graphite and ZnO increases drastically the rate of the carboreduction and conversion of Zinc Oxide. Conversion of 90% can be reached at 1000 °C, 20 min after the start of reaction.

5. THE KINETIC MODEL

A general model for thermal carboreduction of zinc oxide based on the reactions (3)-(4) was developed. The following system of differential equations can be written for the number of moles of the components n_i .The system of equations (5-9) describes the carboreduction under isothermal conditions.

$$\frac{dn_{CO}}{dt} = -(W_r(1+n_{CO}) + (2-n_{CO})W_g + F_{He}n_{CO}) / V_R \qquad (5)$$

$$\frac{dn_{Zn}}{dt} = (W_r(1-n_{Zn}) - W_g n_{Zn} - F_{He}n_{Zn}) / V_R \qquad (6)$$

$$\frac{dn_{CO_2}}{dt} = (W_r(1-n_{CO_2}) - W_g(1+n_{CO_2}) - F_{He}n_{CO_2})/V_R \qquad (7)$$

$$n_{He} = 1 - n_{CO} - n_{Zn} - n_{CO_2} \qquad (8)$$

$$\frac{d\alpha}{dt} = aW_R \qquad (9)$$

W_g *and* W_r are the rates of carbon gasification with CO_2 and reduction of ZnO with CO respectively and F_{He} -is the flow rate of the inert gas, α -the ZnO conversion, V_R -the volume of the reactor.

Mechanism of the reduction of ZnO with CO postulates the irreversible chemisorption of CO on the ZnO lattice with subsequent release of Zn and CO_2 [5]. Reducing gases can attack both the external and internal surface of a ZnO pellet (or particle); the contribution of internal reduction , however, is small for powders or dense pellets such as those used by Guger and Manning [5]. Development of a completely general model for the ZnO reduction process is prohibitively difficult for several reasons. First of all , pellet or particle properties such as external diameter, external and internal surface areas, pore size and so forth, change constantly, thus varying all transport and kinetic resistances. Finally, heat transfer effects are superimposed on this already complex mass transfer problem. To obtain a first approximation model, the following assumption were made: a) internal diffusion is negligible and no cracking of particle or sintering; b) the system is isothermal. The rate of reduction of ZnO in this approximation can be described by a simple equation :

$$W_r = k_r * G_{ZnO} * n_{co} * (1-\alpha)^x , \qquad (10)$$

where *and* G_{ZnO} are rate constant for the ZnO reduction and weight of the ZnO respectively.

The gasification of carbon with CO_2 (reaction 4) proceeds via a two-step oxidation reduction cycle (Walker et al. [4] , Ergun [6] , Strange and Walker [7]). In the first reaction carbon "active free size" is oxidized by CO_2 to carbon-oxygen complexes C(O). These complexes decompose in the rate-determining step to CO. The Langmuir-Hinschelwood theory predicts an equation of the following form for the gasification of carbon with CO_2:

$$W_g = k_g * G_C n_{CO_2} / (1+b\, n_{CO} + b_1 n_{CO_2}) \qquad (11)$$

where k_g is -the rate constant of carbon gasification, G_C -is weight of carbon in the sample, b *and* b_1 are the equilibrium constants.

The system of ordinary differential equations was solved with help of Microsoft Matlab package and corrected according to the experimental data. The following values for the rate constants were obtained: (for mixture of ZnO powder and 1-2 mm activated carbon, after water removing at 500 °C) : k_r = 2.17*10^4*EXP(-24825/RT) cm^3 sec^{-1} g^{-1}, k_g = 0.42*10^{14}*EXP(-61344.4/RT) cm^3 sec^{-1} g^{-1}, $b = 0.0972 * EXP(17540.6/RT)$, b_1=0, x=1.

The following behavior of the reactor temperature during the experiment is assumed:

$$T = 773+(Temp1-773)*(1-EXP(0.07*t)) \qquad (12),$$

where: Temp1-is the temperature in the reactor before the start of the reaction, t-time.
It is assumed that CO and (or) CO_2 are present in the reactor before the start of the reaction. Equations (5)-(12) were solved with different initial conditions in the range of $n^o_{CO} = 10^{-20}$-10^{-4}. The calculations show that the initial conditions can determine only the induction period (like in chain reactions). At temperature of 1000 °C the induction period in the case of $n^o_{CO} = 10^{-20}$ is about 150 sec. This result show that even very small CO concentrations can initiate the reaction. Therefore the equilibrium oxygen pressure can be a source of initial CO concentration. In real systems the induction period is less than 150 sec and the reaction could be initiated by impurities.

Table. 1 shows the experimental and calculated maximum rates of reaction and CO and CO_2 concentrations.

Table 1. Kinetics of carboreduction of zinc oxide. Comparison of experimental and calculated maximum rates of reaction , CO and CO_2 concentrations.

Temp.C	CO		CO_2		Rate of reaction	
	Calcul. % mole	Exper. % mole	Calcul. % mole	Exper. % mole	Calcul. cc/min	Exper. cc/min
1000	0.48	0.5	1.5	0.73	38	40
1100	0.64	0.7	0.4	0.25	75	104
1200	0.82	0.8	0.1	0.16	190	200
1300	0.8	0.72	4*10^{-4}	10^{-4}<	156	120

There is satisfactory agreement between the experimental and calculated data.

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