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THERMOCHEMICAL DECOMPOSITION OF PHOSPHOGYPSUM UNDER H_2-CO_2-H_2O-Ar ATMOSPHERE

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ABSTRACT

The isothermal experiments were carried out in the temperature range 950–1100°C while the Ar gas flow contains 1 to 4%H_2,10%CO_2 and 20%H_2O-vapor.The influence of temperature and partial pressure of H_2 on the phosphogypsum decomposition rate and proceeding reactions were studied.The experimental results can be represented over the temperature range 950–1000°C by Polany-Wigner equation.The activation energy deduced for the process when flow gas contains 1%H_2,10%CO_2,20%H_2O,69%Ar is 20.3 kcal/mol.

INTRODUCTION

In earlier works [1,2,3] on the thermochemical decomposition of phosphogypsum in a different gas atmospheres we had found a very marked dependence of decomposition rate on the specific impurities and gas atmosphere.The proceeding of the reactions 1 and 2 under various gas atmospheres H_2-Ar,H_2-H_2O-Ar and CO-CO_2-Ar have been discussed.

$$CaSO_4 + H_2(CO) = CaO + H_2O(CO_2) + SO_2 \qquad (1)$$
$$CaSO_4 + 4H_2(4CO) = CaS + 4H_2O(4CO_2) \qquad (2)$$

It was shown that both CO_2 and H_2O decrease the contains of CaS in solid product,but P_{H_2O} only slightly affeet the rate of phosphogypsum decomposition.When carrier gas is 4%CO,5–20%CO_2 and Ar, P_{CO_2} inhibits the process and the diffusion became rate determining at higher temperatures.The present work is to continue the above mentioned investigations in the gas atmosphere closer to that from reformed natural gas.

MEASURING METHODS

To get a good corelation between the results of our previous [1,3] and now experiments the same technique and chemical analyses were used.The reactor-mixer of Shimadzu Thermoanalyzer was connected with gas-system consists of gas cylinders,valve regulators, rotameters with fine valve regulators,gas-mixer,apparatures for

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water saturation of gas-mixture.The total flow rate is 335 cc min^{-1}. In such way gas atmosphere contains 1-4%H_2,10%CO_2,20%H_2O and the rest Ar.To have a better regulation,cylinder with H_2-Ar mixture was used.The sample weight is 15 mg and the platinum sample pan is 10mm diameter and 1mm height.Phosphogypsum particles are under 0.1mm and it contains:38.6%CaO,54.7%SO_3,1.5%SiO_2,0.7%P_2O_5,0.7% Fe_2O_3,0.4%Al_2O_3,0.2%MgO.The unsoluble compounds are 2.1%.

RESULTS AND DISCUSSION

The isothermal TG curves of phosphogypsum decomposition at temperature 1100°C in the flow gas:1-4%H_2,10%CO_2,20%H_2O and Ar are shown in Fig.1.It is obvious that decomposition rate is very sensitive to the H_2 in gas phase and especially from 1 to 2%.At this temperature the results are quite close to the experimental data which we got for H_2-Ar and H_2-H_2O-Ar carrier gas[1].The inhibition effect of CO_2 is negligible.Maybe it is due to the surface activation by H_2,which can increase the outflow of CO_2 from the reaction zone.The weight losses and chemical analyses indicate that $CaSO_4$ is completely decomposed to CaO.The straight line logaritmic relationship between the process rate-r and H_2 partial pressure (Fig.3) confirmed the first order reaction as regards H_2.

The isothermal investigation on phosphogypsum decomposition in the temperature range 950-1100°C under gas atmosphere:1%H_2,10%CO_2 20%H_2O,69%Ar(Fig.2)shous that the temperature increases the rate of weight losses to 1050°C.The rate of weight losses at 1050°C and 1100°C is the same.In the solid product at 950°C only a small amount of CaS was found.When at higher temperatures reaction 1 proceeds as a single one and after complete decomposition of phosphogypsum,CaO is a new solid phase.

Experimental results over the temperature range:950-1000°C can be represented by Polany-Wigner[4] equation α=kt,where:α is the degree of decomposition,k-rate constant and t-time.The activation energy deduced for the process under above mentioned atmosphere is 20.3 kcal/mol.It is believed that under the experimental conditions employed,the rate of the process at higher than 1000°C temperatures is controlled by the gas diffusion through the interparticle voids,where the crystal structura of new solid phases takes the main place.From the other point of view the slope of Arrhenius plot (Fig.4) can be due to the increasing of oxigen partial pressure in the reducing environment.Therefrom a complex of investigations as microscope,x-ray and oxygen partial pressure measurements by means of solid electrolyte system are on the way. The thermochemical study of phosphogypsum decomposition under various gas atmospheres has shown that by the regulation of CO,H_2 CO_2 and H_2O partial pressure in the temperature range 950-1100°C the process can be controlled and CaO as a single solid product may be obtained.In the 1%H_2 containing atmosphere the diffusion becomes the rate determining at temperatures above 1000°C,when in a gas flow of 4%CO,10-20%CO_2 and Ar [2,3] it is above 1065°C.The foregoing studies suggest that the transport of the reductive gas to the reaction zone is the process rate determining.Some more complicated gas sistems will be used to make clear the masstransport in the process.

CONCLUSIONS

Thermogravimetric and chemical investigations on the phosphogypsum thermochemical decomposition in H_2-CO_2-H_2O-Ar atmosphere have shown that under the experimental conditions most of the reductive gas is used to form CaO.Only at 950°C a small amounts of CaS in the solid product were found.The inhibition effect of CO_2 in the presence of H_2 is negligiole.The diffusion is a rate determining step at temperatures higher than 1000°C.The experimental results over the temperature range 950-1000°C can be represented by Polany -Wigner equation and the appirant activation energy deduced for the process is 20.3 kcal/mol.

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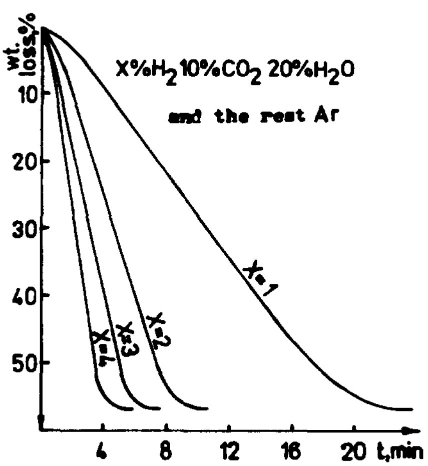

Fig. 1. TG curves for the decomposition of phosphogypsum at 1100°C.

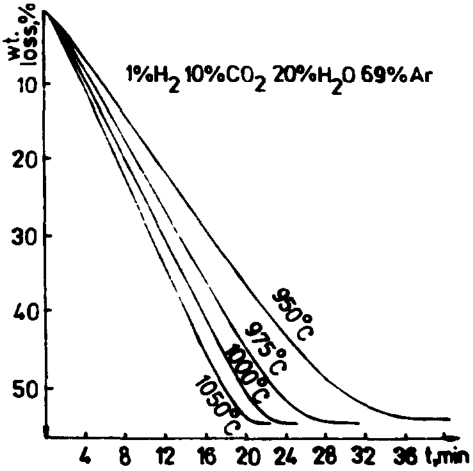

Fig. 2. TG curves for the decomposition of phosphogypsum.

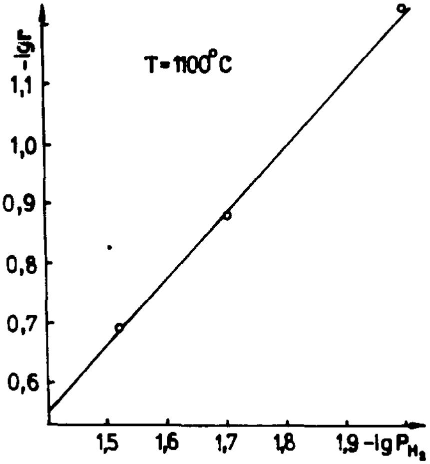

Fig. 3. Dependence of lg r on lgP_{H_2} in the gas atmosphere: 10%CO_2, 20%H_2O, H_2 and Ar.

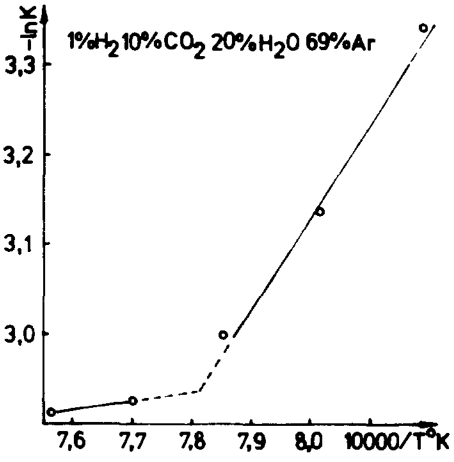

Fig. 4. Arrhenius dependence of lnK on 1/T.