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BARIUM SULPHATE REDUCTION WITH CARBON

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The reduction of $BaSO_4$ by carbon was investigated by means of isothermal thermogravimetric measurements. In combination with a high-temperature thermobalance, solid electrolyte cells were used (i) to purify the N_2 flow gas, and (ii) to measure the partial pressure of oxygen ($CO:CO_2$ ratio, respectively) in the outlet gases.

Mass loss curves and p_{O_2} in the outlet gases were recorded at 743–955 °C. The activation energy of the process was calculated from the isothermal TG curves. X-ray diffraction and SEM showed that the solid product in the whole temperature interval comprised only cubic BaS.

The decomposition of barites by solid carbon-containing reducers has been investigated by many authors under various experimental conditions [1, 2]. Though it is generally accepted that the solid reducers are initially gasified to CO, which interacts with $BaSO_4$, the experimental data verifying this mechanism are rather scanty [2, 3]. The literature provides no data on the decomposition of $BaSO_4$ by solid reducers in a gaseous medium with a controlled oxygen partial pressure p_{O_2} in the gas phase.

The present paper reports a thermogravimetric investigation of the process of decomposition of $BaSO_4$ by pure carbon in a nitrogen stream with simultaneous control of p_{O_2} in the gas phase.

Pure carbon (99.5% C) and reagent grade barium sulphate heated at 700° were used in the investigations. The mixtures were prepared in a nitrogen atmosphere by homogenization for 6 hours.

The kinetic studies were carried out in the set-up outlined in Fig. 1. Isothermal gravimetric measurements were performed with a Shimadzu–31H electronic balance. The carrier N_2 gas with a flow rate of 65 cm^3/min was purified from oxygen with a solid electrolyte pump and the water vapour was eliminated with P_2O_5. Simultaneously, p_{O_2} in the initial gases was measured continuously with a $CaO–ZrO_2$ solid electrolyte system.

All experiments were carried out with a mullite crucible (internal diameter 8 mm): the sample weight was 100 mg, with a predominant particle size of

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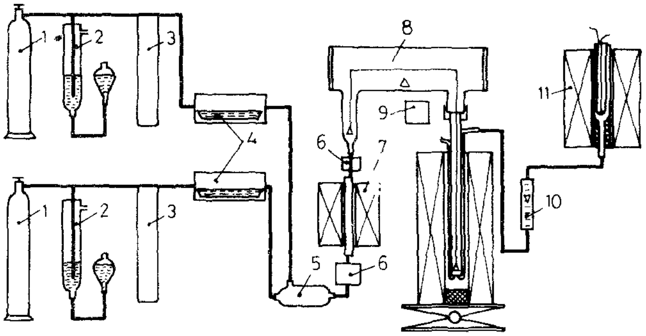

Fig. 1 Experimental apparatus
1 – cylinders; 2 – manostates; 3, 10 – rheometers; 4 – P_2O_5 dryers; 5 – mixer; 6 – liquid N_2 dryer; 7 – oxygen pump; 8 – microbalance; 9 – blower; 11 – P_{O_2} EMF cell

60–70 μm. The solid products prepared were subjected to X-ray phase analysis, and their barium sulphate contents were determined.

A mixture of barium sulphate and carbon with a mole ratio C: $BaSO_4$ = 2.5 was investigated in the temperature range 743–955°. The results from the preliminary experiments revealed that the selected mole ratio permits the complete reduction of barium sulphate to barium sulphide. With the aim of obtaining information regarding the mechanism of $BaSO_4$ reduction, the N_2 carrier gas was subjected to

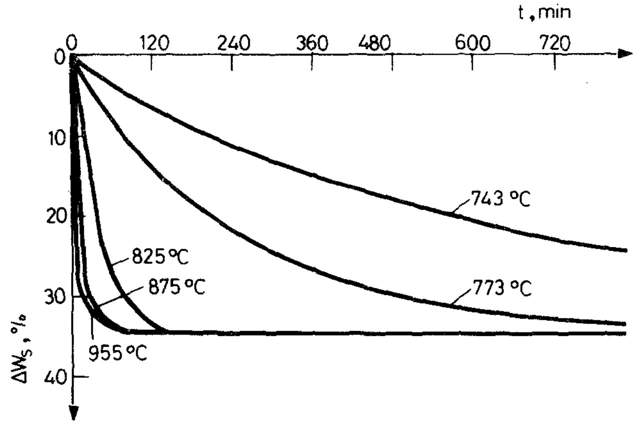

Fig. 2 TG-curves of isothermal decomposition
Sample weight = 100 mg,
Mol ratio C : $BaSO_4$ = 2.5,
Flowrate N_2 = 65 cm^3 min^{-1},
Inlet gas P_{O_2} = 10^{-14} atm

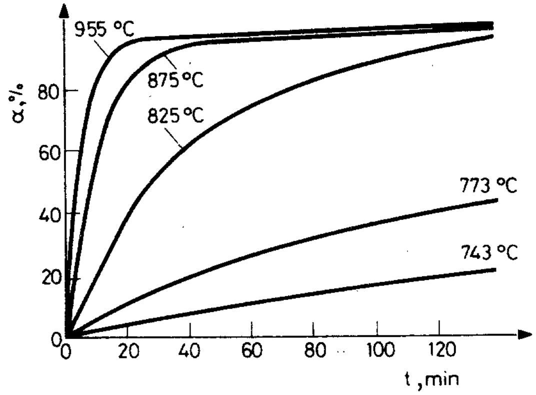

Fig. 3 Kinetic curves of isothermal decomposition
Sample weight = 100 mg,
Mol ratio C : $BaSO_4 = 2.5$,
Flowrate $N_2 = 65$ cm^3 min^{-1},
Inlet gas $P_{O_2} = 10^{-14}$ atm

thorough purification from oxygen to a p_{O_2} in the range 10^{-13}–10^{-14} atm, i.e. p_{O_2} was very close to its equilibrium value for the system C–CO–CO_2.

The isothermal gravimetric curves depicting the variation of the sample mass with time for different temperatures, and the kinetic curves of the degree of decomposition *vs.* time are presented in Figs 2 and 3. The temperature effect on the processes kinetics is exhibited particularly strongly in the range 723–825°. Thus, while 48 hours is required for complete $BaSO_4$ reduction at 743°, about 3 hours is required at 825°, and less than 2 hours in the range 875–955°. The kinetic parameters of the process were obtained by treating the data in Fig. 3 by means of the Kekam equation (Fig. 4) and the Arrhenius equation. The activation energy obtained, 10.26 kcal mol^{-1}, was about one-third of that for the same process carried out under the same conditions, but using as the carrier gas N_2 in which $p_{O_2} \sim 10^{-5}$ atm and $p_{H_2O} \sim 10^{-4}$ atm. It is obvious that p_{O_2} and p_{H_2O} have a definite effect on the kinetics of $BaSO_4$ reduction with solid carbon, although their values are quite low, 10^{-4}–10^{-14} atm.

The experimental set-up permits practically simultaneous measurement (with a time delay of less than a second) of the values of p_{O_2} in the gas phase. Figure 5 shows the dependence of p_{O_2} on time for the first 40 min at different temperatures. At temperatures above 743°, the variation of p_{O_2} in the gas phase was the most significant for the first 1–2 min, after which it equalized with p_{O_2} in the carrier gas. At 743°, this equalization occurs after a period of 30 min. The four curves in Fig. 5 are characterized by a rapid p_{O_2} decrease, followed by a rapid increase and a new decrease, after which the above-mentioned equalization is reached in the

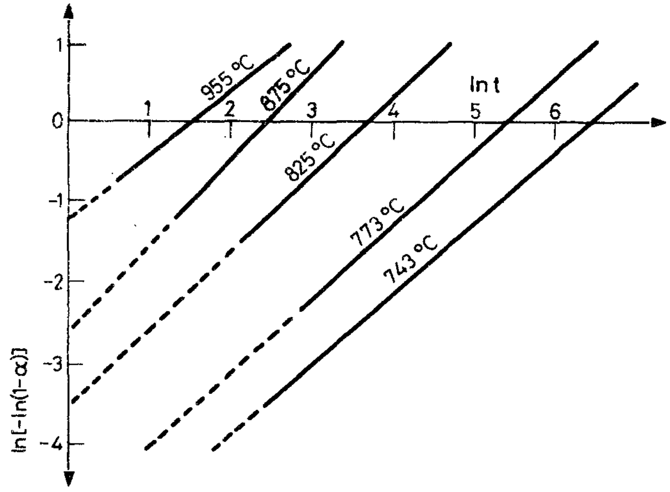

Fig. 4 $-\ln[-\ln(1-\alpha)]$ *vs.* $\ln t$ plots at different temperatures

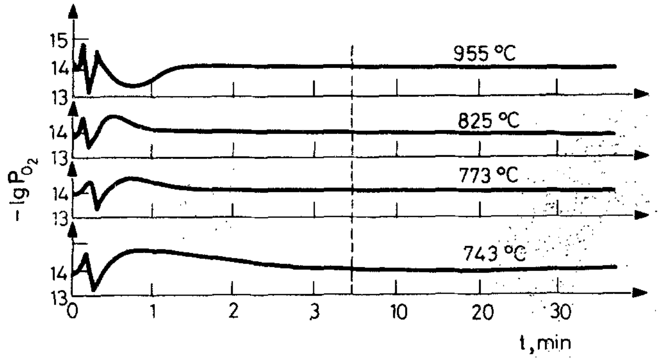

Fig. 5 The variation of P_{O_2} with time

temperature range 743–825°. At 955°, this equalization is observed after a repeated slower increase and decrease of p_{O_2}. The established sequential changes of the oxygen potential are associated with rapid changes in the reaction mixture at the beginning of the reduction process. The initial rapid p_{O_2} decrease is most probably due to the processes of adsorption and chemisorption of oxygen, while the rapid p_{O_2} increase is determined by the occurrence of several reactions:

$$BaSO_4 \rightleftarrows BaS + 2\,O_2 \tag{1}$$

$$BaSO_4 + 2\,C \rightleftarrows BaS + 2\,CO_2 \tag{2}$$

$$BaSO_4 + 4\,C \rightleftarrows BaS + 4\,CO \tag{3}$$

$$CO_2 + C \rightleftarrows 2\,CO \tag{4}$$

$$CO_2 \rightleftarrows CO + 0.5\,O_2 \tag{5}$$

$$CO_2 \rightleftarrows C + O_2 \tag{6}$$

$$BaSO_4 + 4\,CO \rightleftarrows BaS + 4\,CO_2 \tag{7}$$

The second p_{O_2} decrease is most probably due to the dominating effect of reactions (3) and (4) for a definite period of time, after which reaction (7) predominates. The temporary higher p_{O_2} at 955° is explained by the rapid accumulation of carbon dioxide in the system from reaction (7) and the establishment of equilibrium in reactions (4–6). The duration of the initial period depends on the temperature, as the reaction degree does not exceed 10%. Further, the development of the process is outlined by the establishment of a constant oxygen potential determining the constancy of the ratio $p_{CO}:p_{CO_2} = 0.13\text{–}0.20$. This fact motivates the conclusion that the reduction process proceeds mainly with a definite ratio of the rate constants of reactions (1–7) for the range of temperatures investigated.

Conclusion

The established regularities support the assumption of a significant gas phase composition effect on the kinetics of $BaSO_4$ reduction with solid carbon. The simultaneous application of thermogravimetric analysis and solid electrolyte systems for purifying and measuring p_{O_2} in the gas phase permits additional information on the process mechanism. The experimental set-up could be successfully applied for kinetic studies of similar processes.

References

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Zusammenfassung — Die Reduktion von $BaSO_4$ mit Kohlenstoff wurde durch isotherme thermogravimetrische Messungen verfolgt. Mit einer Hochtemperatur-Thermowaage wurden Festelektrolyten kombiniert (1) zur Reinigung des Spülgases N_2 von Sauerstoff, (2) zur Messung des O_2-Partialdruckes (bzw. des Verhältnisses $CO:CO_2$) im entweichenden Gas. Die Gewichtsverlust- und Sauerstoffpartialdruck-Kurven bei 743—955 °C wurden aufgezeichnet. Aus den TG-Kurven wurde die Aktivierungsenergie des Prozesses berechnet. Im gesamten untersuchten Temperaturbereich entstand als festes Reaktionsprodukt nach Röntgenbeugungs- und SEM-Untersuchungen nur kubisches BaS.

Резюме — Изотермической термогравиметрией изучено восстановление сульфата бария углеродом. Твердоэлектролитные ячейки в комбинации с высокотемпературными термовесами были использованы для очистки азота, как газа-носителя, и для измерения парциального давления кислорода (соотношения $CO:CO_2$) в выходных газах. В температурном интервале 743—955° измерены кривые в координатах потеря веса — парциальное давление кислорода (P_{O_2}) в отходящих газах. Из изотермических кривых ТГ была вычислена энергия активации процесса. Ретгенофазовым анализом было установлено, что во всем температурном интервале образовывался сульфид бария с кубической структурой.