Thermochimica Acta, 58 (1982) 333–339
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

THE REDUCTION OF PYROLUSITE IN A HYDROGEN ATMOSPHERE

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(Received 13 April 1982)

ABSTRACT

The isothermal reduction of pyrolusite, β-MnO_2, in a hydrogen atmosphere has been studied. Under these conditions the reduction product is Mn_3O_4. The kinetics of the reaction were determined and the activation energy for the process was calculated to be 140.0 kJ mole^{-1}.

INTRODUCTION

The minerals pyrolusite (β-MnO_2), and manganite (γ-MnOOH) are frequently found in the same ore bodies with identical morphologies in spite of having different structures (pyrolusite is tetragonal, rutile type, and manganite is monoclinic, type InOOH). Both species are even, on occasions, found forming part of the same mineral specimen [1]. This suggests that it might be possible to transform pyrolusite to manganite by means of reduction in the solid state using hydrogen as the reducing agent. This occurs in the system [2]

$$2\ CrO_2(s) + H_2(g) \rightarrow 2\ CrOOH(s)$$

which is structurally analogous.

However, under the conditions of this study, the reaction product was, in every case, hausmannite, Mn_3O_4, with a spinel type structure. In the present paper the transformation kinetics are studied and a reaction model consistent with these results is proposed.

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0040-6031/82/0000–0000/$02.75

EXPERIMENTAL

The reductions were carried out at 280, 290 and 300°C with a hydrogen pressure of 400 mm Hg in a gravimetric apparatus equipped with a Cahn RG electrobalance and a regulated two-body furnace which maintained both pans at the same temperature. The equipment has a vacuum system capable of reaching pressures of between 10^{-5} and 10^{-6} mm Hg. Pressure measurements were made using Bell and Howell pressure transducers.

The starting material was a pyrolusite of mineral origin from Germany. Chemical analysis of this material by the bismutate method [3,4] indicated a composition of $MnO_{1.99}$, and X-ray diffraction showed only the spacings characteristic of β-MnO_2. The quantity of sample used in all the experiments was 50 mg and the reduction product was identified by X-ray diffraction as Mn_3O_4. The fraction reacted was determined from the weight loss during the process

$$3\,MnO_2(s) + 2\,H_2(g) \rightarrow Mn_3O_4(s) + 2\,H_2O(g)$$

The evolution of the porous texture during the reaction was studied as follows. The starting material was exposed to the action of the reducing gas at 290°C. Once the process was initiated, the reaction was frozen by evacuating the vessel and the N_2 adsorption–desorption isotherms at 77 K were determined on the partially reduced product. A similar determination was realized on the initial samples after degasification. The gases used in all the experiments were of 99.99% purity.

RESULTS

Figure 1 shows the reduction isotherms obtained under the conditions described. The kinetic analysis was carried out by the method proposed by Sharp et al. [5], and good agreement was found with the kinetic equation

$$1-(1-\alpha)^{1/3}=kt$$

corresponding to the contracting sphere kinetic model, as shown in the straight lines obtained in Fig. 2 where this equation is represented. The gradients of these lines were found to be 0.0101 (280°C), 0.0178 (290°C) and 0.0293 (300°C) min^{-1}. From these values, by applying the Arrhenius equation, the activation energy of the process was determined as $E = 140.0$ kJ mole^{-1}. The initial stage of the process, corresponding to the nucleation and growth of nuclei, was shown to follow a power law of the type

$$\alpha = kt^3$$

by plotting $\ln \alpha$ against $\ln t$ (Fig. 3) for values of the fraction reacted of between 0 and 0.2. The gradients of these straight lines have values of 3.31 (280°C), 3.01 (290°C) and 2.98 (300°C).

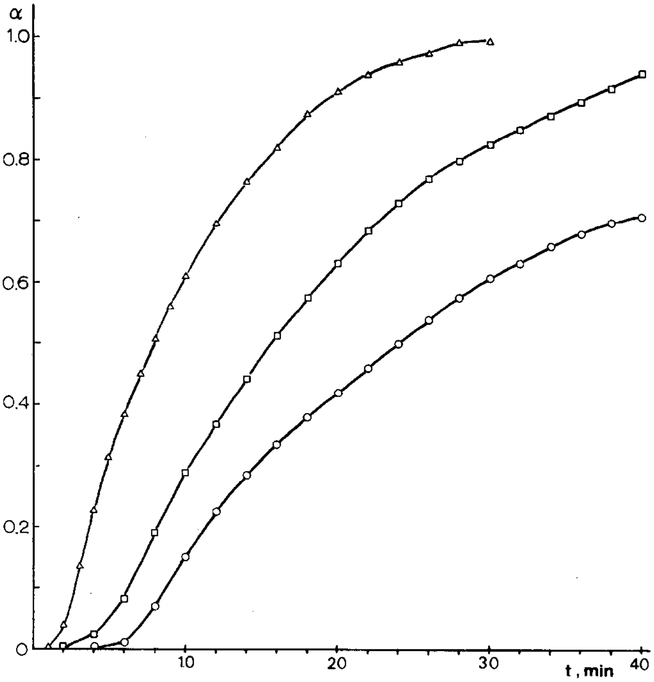

Fig. 1. Reduction isotherms of pyrolusite with hydrogen. ○, 280°C; □, 290°C; △, 300°C.

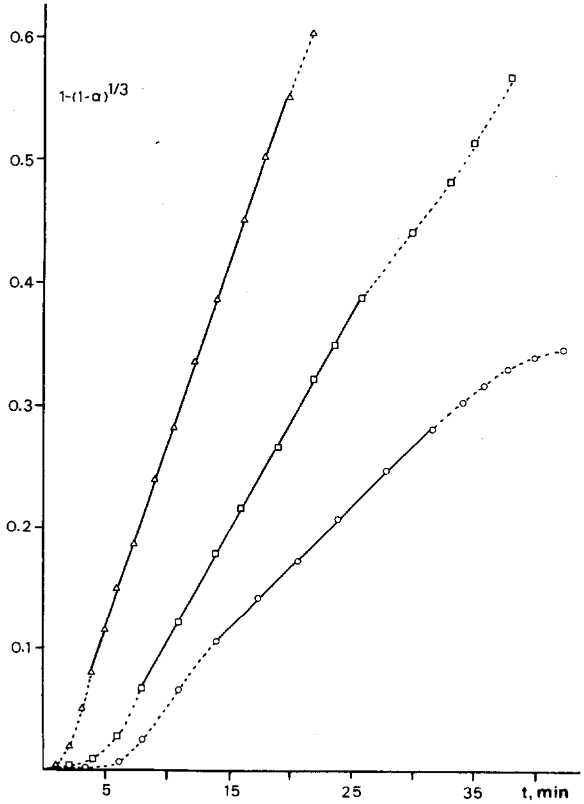

Fig. 2. $1-(1-\alpha)^{1/3}$ as a function of time. ○, 280°C; □, 290°C; △, 300°C.

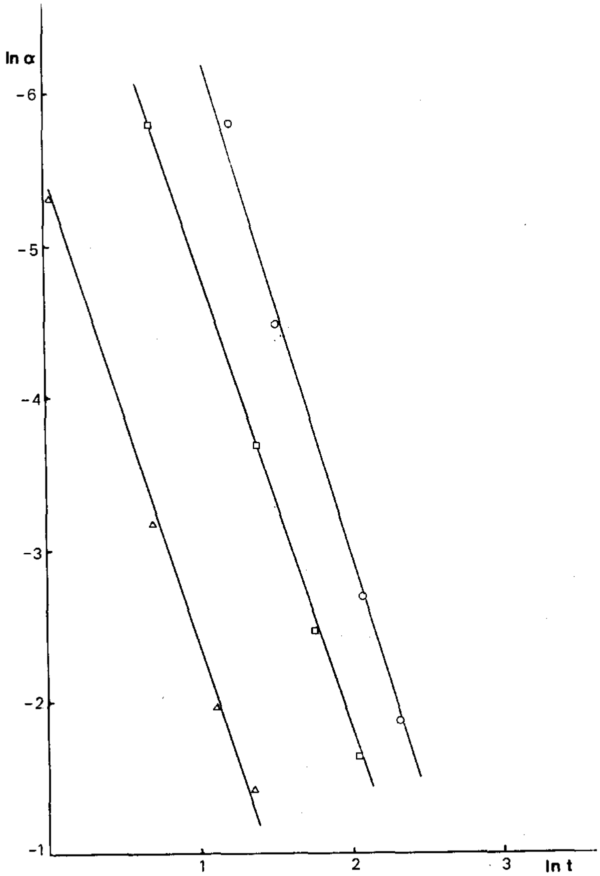

Fig. 3. lnα as a function of ln t. ○, 280°C; □, 290°C; △, 300°C.

Figure 4 shows the N_2 adsorption–desorption isotherms at 77 K determined on the initial sample ($\alpha = 0$) and on three partially reduced samples with $\alpha = 0.27$, 0.59 and 0.88. These isotherms are intermediate between types II and IV of the B.D.D.T. [6] classification and show hysteresis loops, which suggests the existence of mesopores. Pierce's [7] method was used to obtain the distribution of pore radii and these are given in Fig. 5.

DISCUSSION AND CONCLUSIONS

The distribution of pore radii (Fig. 5) indicates the existence of a marked porosity in the starting material, corresponding to pores of radii close to 2.2 nm. During the reduction process these pores decrease in size while larger pores with radii between 3.0 and 8.0 nm are formed. The maximum porosity

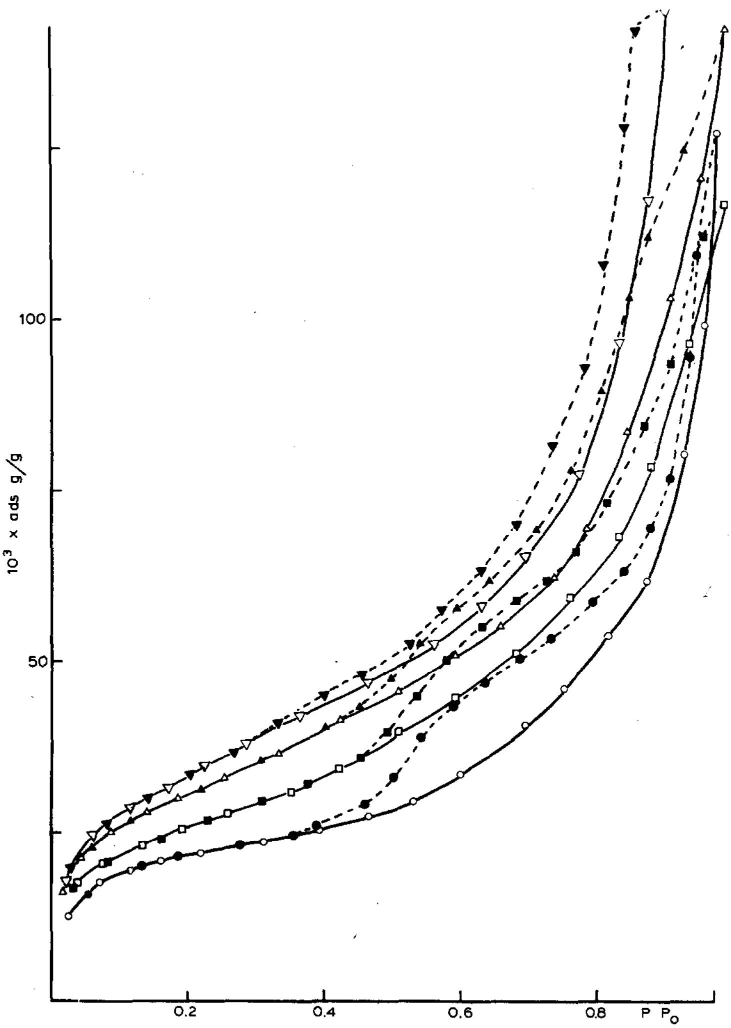

Fig. 4. N_2 adsorption–desorption isotherms at 77 K on partially reduced pyrolusite. ○, $\alpha=0$; □, $\alpha=0.27$; △, $\alpha=0.59$; ▽, $\alpha=0.88$. The black symbols correspond to the desorption branch.

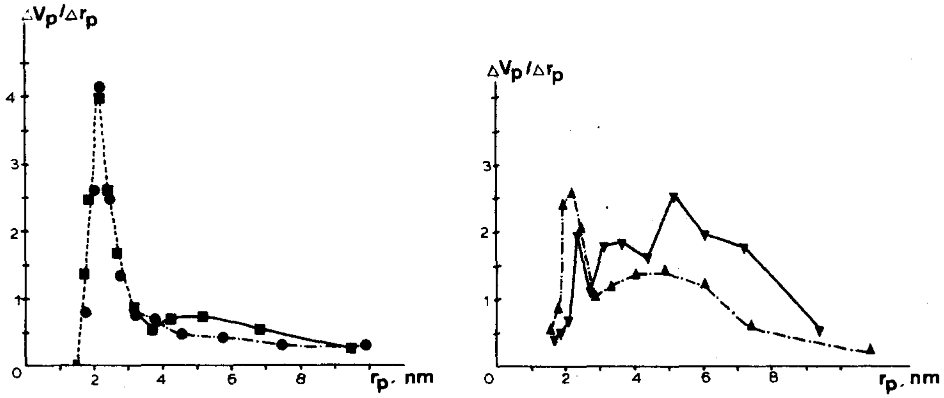

Fig. 5. Pore radii distribution for samples of partially reduced pyrolusite. ●, $\alpha=0$; ■, $\alpha=0.27$; ▲, $\alpha=0.59$; ▼, $\alpha=0.88$.

corresponds to $r = 5.0$ nm. These results seem to indicate that the larger pores have formed at the expense of the smaller initial ones, which suggests that the reaction starts at the walls of these pores. A reaction model for the process which could explain all the results obtained could be as follows. The reaction begins with an instantaneous nucleation on the walls of the pores which are readily accessible to the reducing gas since the reduction does not seem to be controlled by diffusion phenomena. These nuclei start to grow in three dimensions which would give, assuming the interface to be hemispherical of radius r, the fraction reacted as proportional to the radius cubed

$$\alpha = ar^3$$

Given a constant interface advance velocity

$$G = \frac{\mathrm{d}r}{\mathrm{d}t}$$

the rate of the reaction would be

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = 3\, Ga^{1/3}\alpha^{2/3}$$

which on integrating leads to an expression of the type

$$\alpha = G^3at^3 = kt^3$$

which is in agreement with the results obtained during the first stage of the process.

However, if the walls of the pores are sufficiently close together, the interaction of the nuclei will result in the isolation of large blocks of the reacting material and will cause a contraction of the interface. This is shown in Fig. 6. If r_0 is the initial radius of this portion ($t = t_0$) which is assumed to be ideally spherical, and $r_1 < r_0$ the radius after time t, the fraction reacted in this interval will be

$$\alpha = \frac{r_0^3 - r_1^3}{r_0^3}$$

and again assuming a constant interface advance velocity

$$G_1 = \frac{-\mathrm{d}r}{\mathrm{d}t}$$

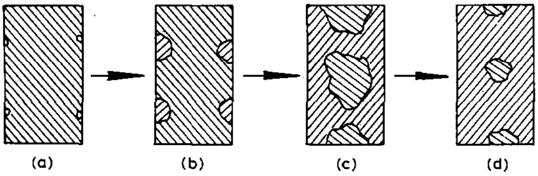

Fig. 6. Schematic representation of the course of the reaction. Nucleation and growth (a) and (b); contraction of the interface (c) and (d).

gives

$$\frac{d\alpha}{dt} = \frac{3\,G_1}{r_0}(1-\alpha)^{2/3}$$

which on integrating leads to

$$1-(1-\alpha)^{1/3} = \left[1 - G_1\frac{t_0}{r_0} - (1-\alpha_0)^{1/3}\right] + \frac{G_1}{r_0}t$$

and as G_1, r_0, t_0 and α_0 are constant, this becomes

$$1-(1-\alpha)^{1/3} = a + bt$$

which is in agreement with the experimental results. According to this equation, the activation energy calculated from the values of the gradient b will correspond to the advance of the interface in this stage of the process.

REFERENCES

1 O.P. Bricker, Am. Mineral., 50 (1965) 1296.
2 R. Saez Puche and M.A. Alario Franco, An. Quim., 76 (1980) 229.
3 W.J. Blum, J. Am. Chem. Soc., 74 (1952) 1379.
4 A. Jerez, Memoria de Licenciatura, Universidad Complutense, Madrid, 1973.
5 J.H. Sharp, G.W. Brindley and B.N.N. Achar, J. Am. Ceram. Soc., 49 (1966) 379.
6 S. Brunauer, L.S. Deming, U.S. Deming and E. Teller, J. Am. Ceram. Soc., 62 (1940) 1723.
7 C. Pierce, J. Phys. Chem., 57 (1953) 149.