

THERMAL DECOMPOSITION AND REDUCTION OF CrO₂ TO CrOOH

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ABSTRACT

We present in this paper a study of the influence of porous texture in the reduction of CrO₂ by hydrogen. The porous texture is itself dependent on the decomposition of CrO₂ to Cr₂O₃. When this decomposition is below ~ 7%, the porosity enhances the reduction rate. However, for decomposition over ~ 7% sintering starts and the reduction reaction becomes slower.

INTRODUCTION

It has recently been shown [1] that the topotactic reduction of small, prismatic single-crystalline particles of CrO₂ [2,3]



occurs by means of a unidimensional diffusion mechanism in which the hydrogen diffuses along the empty tunnels that are parallel to the tetragonal axis in the rutile-type structure of CrO₂ [4]. In agreement with this mechanism, the kinetics of the process represented in eqn. (1) can be fitted to the parabolic equation [5], from which the diffusion coefficient of hydrogen in chromium dioxide can be expressed as

$$D = 10^{-6} \exp(-19 \pm 2/RT) \text{ cm}^2 \text{ s}^{-1} \quad (2)$$

This equation appears to be valid within the limits $490 < T < 520$ K and $30 < P_{\text{H}_2} < 110$ Torr [1].

In the course of this work, it has been observed that the average crystal length, τ , as determined by electron microscopy, has a marked influence on both the amount of reduction and the extent of decomposition experienced by CrO₂ in the process of attaining the reduction temperature. Actually, this decomposition process [1,6–9], which can be expressed as



is a very complex one [10–12]. The behavior of CrO₂ towards reduction by

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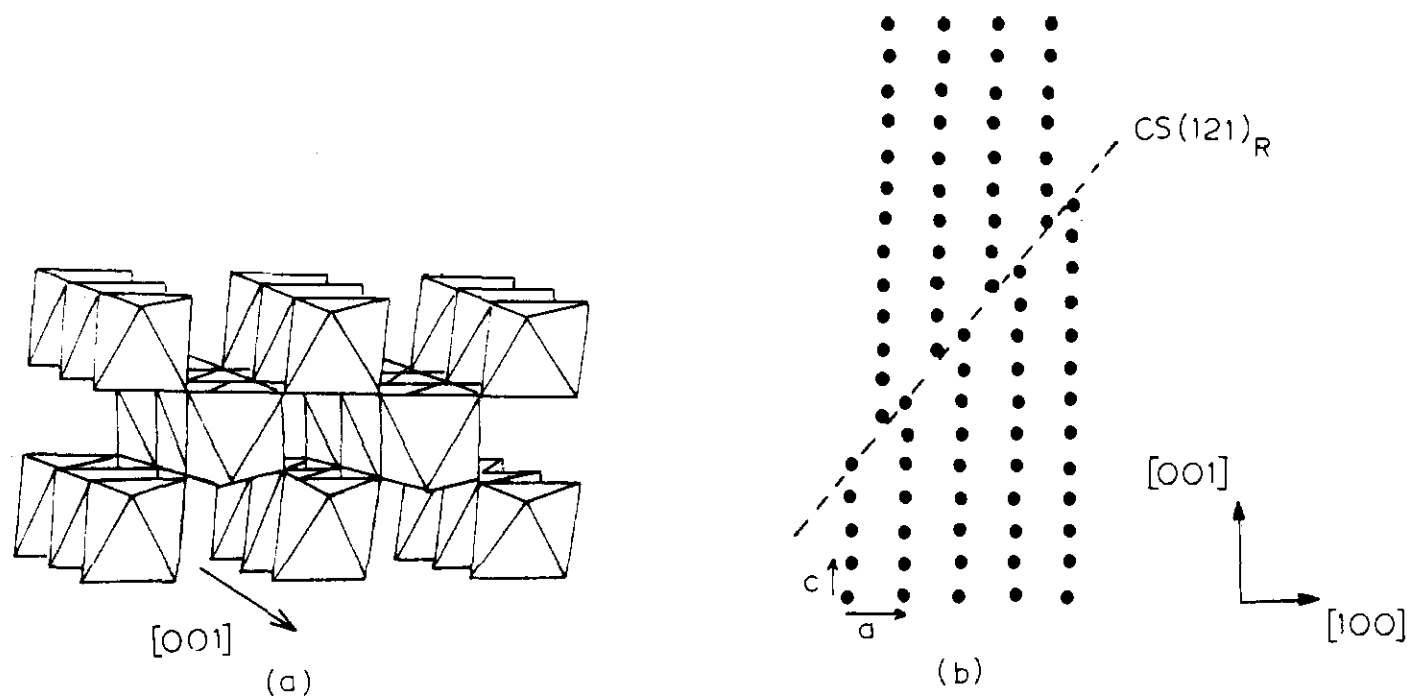


Fig. 1. (a) Perspective view of the rutile structure showing the empty crystallographic tunnels parallel to the c-axis. (b) Idealised projection along $(010)_R$ of the metallic positions in the rutile structure, showing that the above tunnels are closed by the presence of crystallographic shear planes (CS).

hydrogen has been explained [13] by the consecutive formation of crystallographic shear planes in the $(121)_R$ orientation of the rutile-type unit cell and/or a porous texture.

The first of these two processes, namely the formation of crystallographic shear planes [14], close up the empty "chimneys" [15] parallel to the c-axis of the unit cell as shown in Fig. 1. The second process will open up a series of empty spaces that may allow the hydrogen to circumvent the crystallographic shear barriers.

In order to further explore this process, we have studied the hydrogen reduction of several samples of CrO_2 of homogeneous size and shape and different average length, partially decomposed at temperatures higher than the reduction temperature. The result of such a study is described and discussed.

EXPERIMENTAL

Samples of CrO_2 were supplied by R.C.A. laboratories (U.S.A.). They were formed of small single-crystalline prismatic particles with an acicularity ratio of the order of 10/1 (Fig. 2). Average particle length, τ , ranging from 0.250 to 0.430 μm , was determined by electron microscopy, while electron diffraction demonstrated that the c-axis was parallel to each particle's longest dimension.

The surface areas (BET areas [16]) have been determined on a conventional volumetric apparatus [16] by the adsorption of nitrogen at its boiling point [12].

The starting materials and their reaction products were also characterized

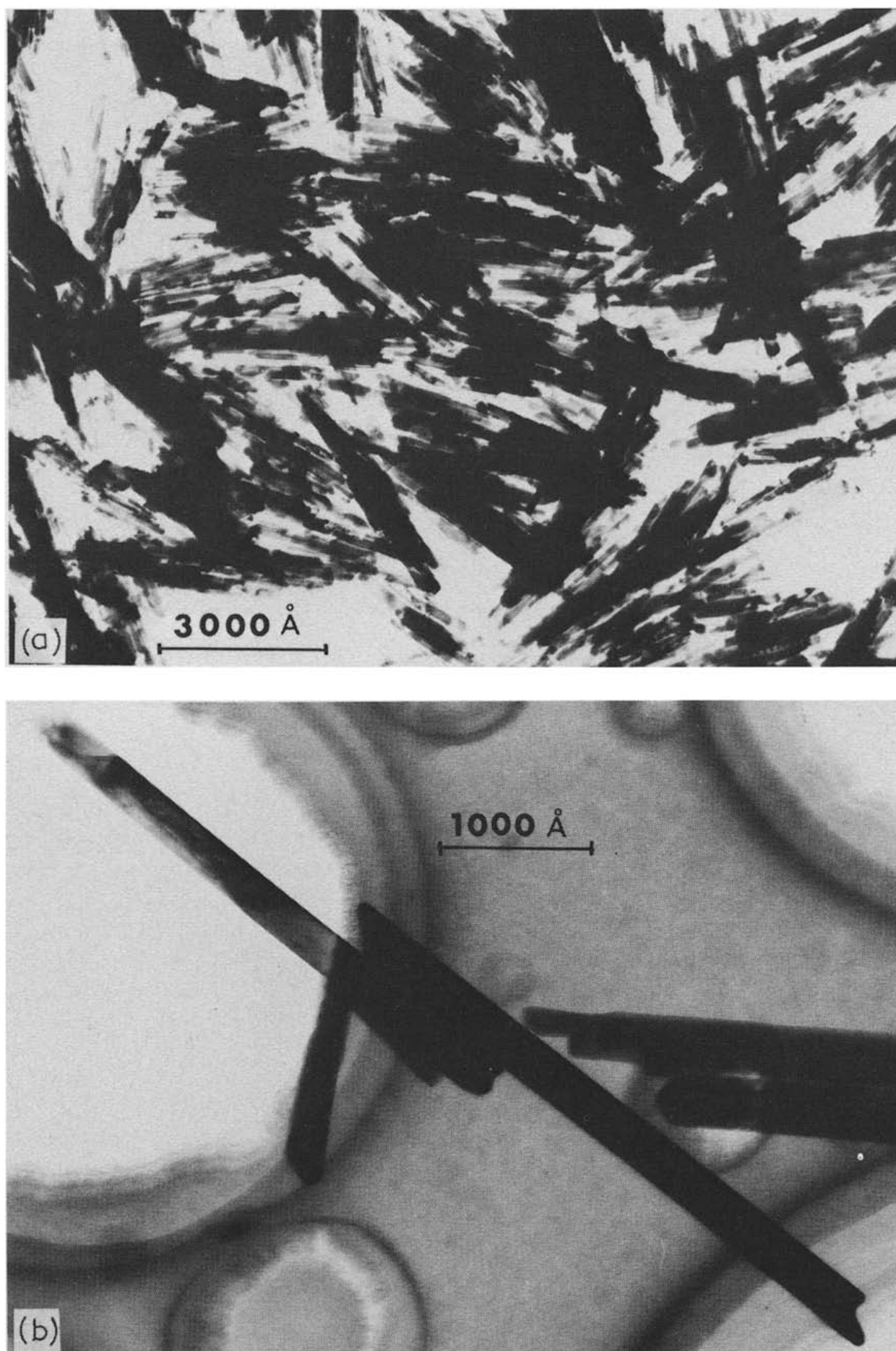


Fig. 2. Electron micrograph of untreated CrO_2 . (a) General view. (b) Enlarged area showing the prismatic crystal morphology.

by X-ray diffraction. This work was performed on a Philips PW-1310 diffractometer with nickel-filtered CuK_α radiation. Electron microscopy and diffraction were made on a Siemens Elmiskop 102 microscope operated at 100 kV.

Reduction experiments were performed on a home-made thermogravimetric apparatus [17] based on a Cahn electrobalance, after the design of Cutting [18]. Powder samples (~ 90 mg) were treated at a controlled temperature in a vacuum better than 10^{-4} Torr until a certain decomposition, P_D , was obtained; P_D is the percent decomposition corresponding to eqn. (3) and its maximum value is 9.6%. Subsequently, each sample was equilibrated for 1 h at the reduction temperature while still under vacuum. Hydrogen of high purity (99.9995%) was then introduced into the system. The amount of reduction attained in each experiment, α_F , was determined by its weight gain according to eqn. (1); $\alpha_F = 1$ corresponds to the total reduction. Full details of these procedures have been given earlier [1,12,13].

RESULTS AND DISCUSSION

Figure 3 shows an example of the reduction isotherms corresponding to the CrO_2 sample having $\tau = 0.348 \mu\text{m}$, decomposed to different extents and subsequently reduced at $T = 536$ K and $P_{\text{H}_2} = 150$ Torr. The influence of the predecomposition of the sample is clear in both reduction rate, as approximated by the slope of these α/t plots, and final reduced state α_F . In this way, for a predecomposition of 4.7%, the final state was fully reduced ($\alpha_F = 1$) and was attained in about 50 min. Predecomposition up to 1% required 150 min, i.e., three times longer to attain constant weight in reduction, corresponding to $\alpha_F = 0.80$. Similar results were obtained for all the samples. Table 1 collects the data corresponding to three samples of

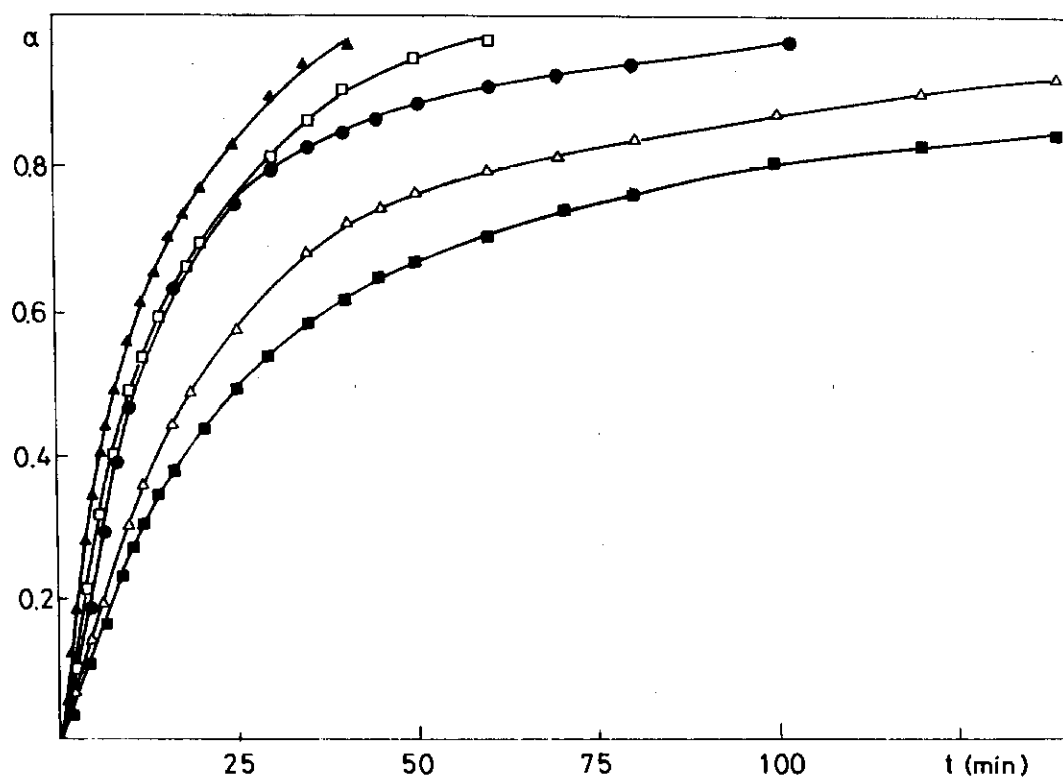


Fig. 3. Reduction isotherms for the sample with $\tau = 0.348 \mu\text{m}$. P_D (%): ■, 1.0; △, 2.1; ●, 3.6; ▲, 4.7; □, 6.5.

TABLE 1

Reaction parameters in the reduction of CrO_2 by hydrogen at 536 K and $P_{\text{H}_2} = 150$ Torr

τ (μm)	T_D (K)	P_D (%)	$t_{0.5}$	α_F
0.250	536	1.1	23.5	0.64
	688	2.1	20	0.77
	706	3.8	5	1
	745	6.0	5.5	1
0.348	630	1.0	25	0.83
	685	2.1	19	0.92
	718	3.6	11	0.98
	756	4.7	8	1
	770	6.5	10	1
0.431	536	0.5	47	0.67
	693	2.0	27.5	0.97
	745	4.0	11	1
	758	5.8	7	1

τ = Average particle length; T_D = partial decomposition temperature; P_D = percent decomposition of CrO_2 according to eqn. (3); $t_{0.5}$ = half-reaction time (time to reach $\alpha = 0.5$); α = degree of reduction; α_F = final degree of reduction.

different particle size and differing in τ by about 1000 Å. Such samples were also reduced at $T = 536$ K and $P_{\text{H}_2} = 150$ Torr.

The marked increase observed in the reactivity towards hydrogen can be attributed to the evolution of the porous texture of CrO_2 in the decomposition reaction. As stated above and discussed in detail elsewhere [11,19], the thermal decomposition of CrO_2 produces a porous texture the extent of which is very much dependent on the amount decomposed and also depends on the atmosphere in which the decomposition is carried out. We have observed that, as expected, decomposition under vacuum generates a larger surface area and a greater pore volume than decomposition in air [19]. In this way, the $\tau = 0.348$ μm sample, which was initially impervious towards the adsorption of nitrogen, and had a BET area of $15.2 \text{ m}^2 \text{ g}^{-1}$, developed a pore volume of $9.6 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$ after decomposition at 700 K, to $\sim 3.6\%$. A similar treatment in air produced a pore volume of about one third of that generated under vacuum.

The presence of this porosity which, as shown in Fig. 4, can be observed by means of electron microscopy, is undoubtedly responsible for the progressive increase in reactivity observed in Fig. 3 and, more generally, in Table 1. These pores, which are perpendicular to the crystallographic c-axis, provide the hydrogen with free access to the crystallographic tunnels existing in the structure of CrO_2 even if, as discussed previously [13], they are occasionally interrupted by the presence of crystallographic shear planes. However, there is a limit in the maximum pore volume that can be attained, and it appears from our work that, when the degree of decomposition, P_D , reaches $\sim 7\%$,

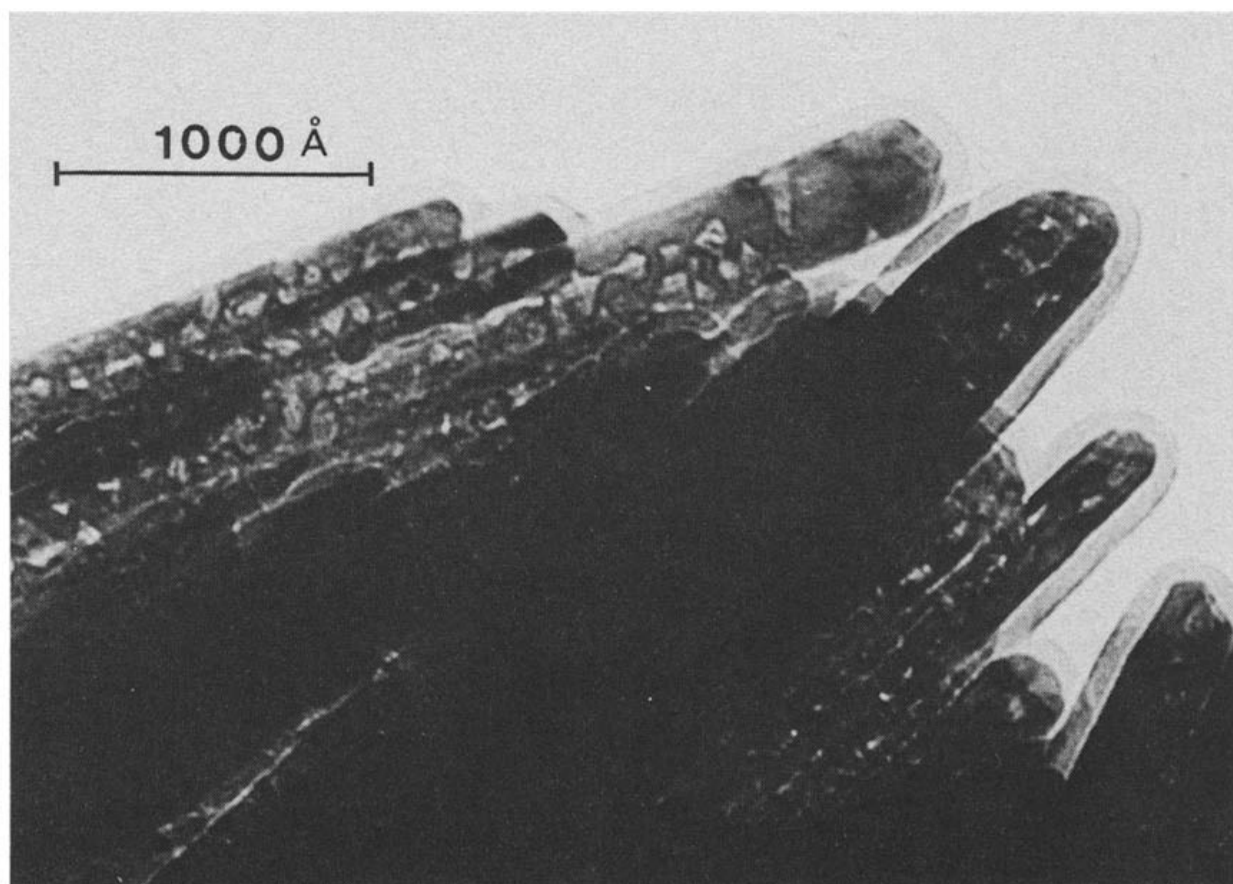


Fig. 4. Electron micrograph of the $\tau = 0.348 \mu\text{m}$ sample treated at 700 K under vacuum.

both the pore volume and the surface area experience a very marked decrease. In this way, in the case of the sample with $\tau = 0.348 \mu\text{m}$, the BET area was only $6.5 \text{ m}^2 \text{ g}^{-1}$ after treatment in air at 1073 K. Such a marked decrease in the magnitude of the textural parameters is due to the beginning

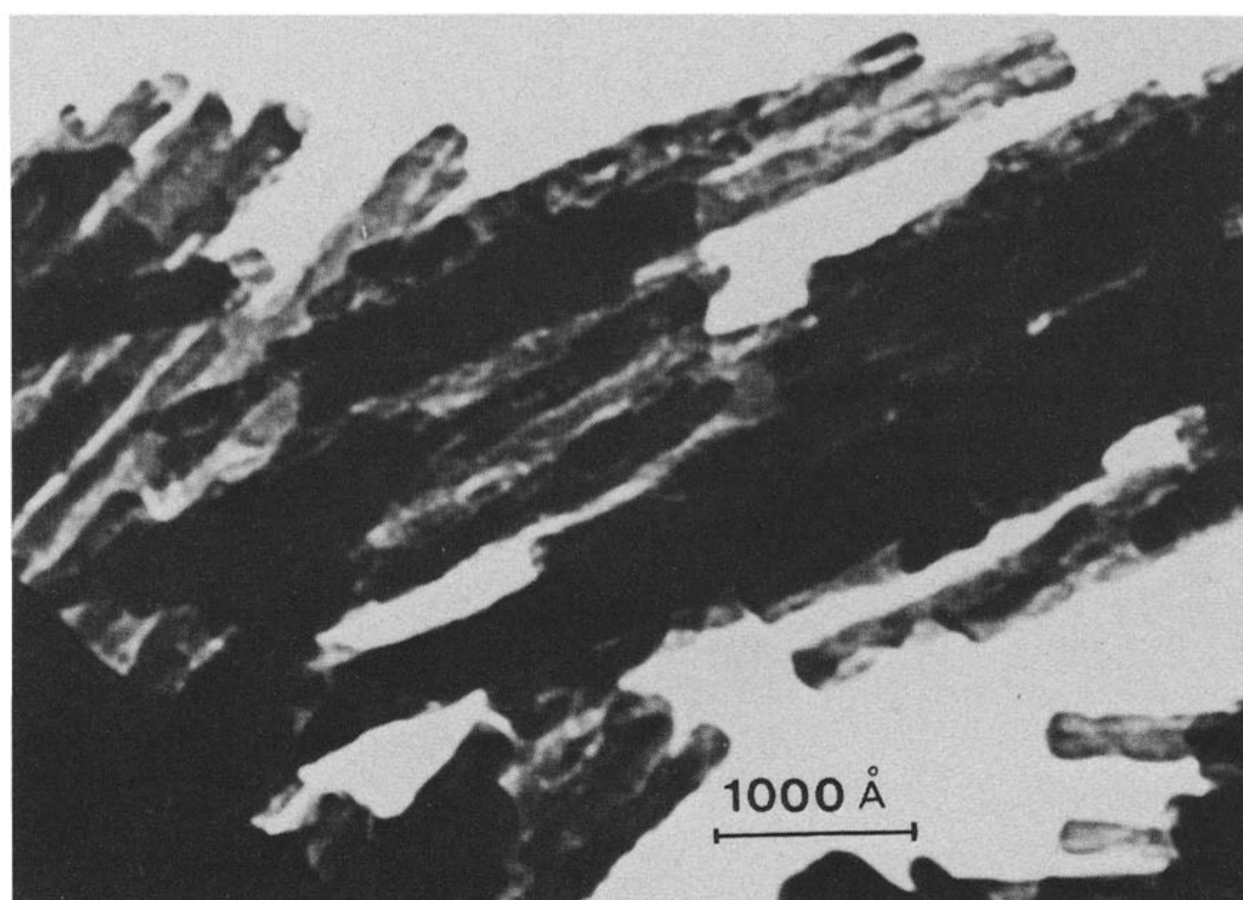


Fig. 5. Electron micrograph of the sample with $\tau = 0.348 \mu\text{m}$ heated in air at 1073 K.

of the sintering process which closes the pores generated in the earlier stages of the decomposition. Figure 5 shows an electron micrograph of a sample heated in air at 1073 K; it can be seen that the particles have rounded edges and weld together, a process that inevitably produces a decrease in surface area and porosity and consequently produces a lowering of the accessibility of the crystallographic tunnels to the hydrogen. This explains the decrease observed in the reaction rate when P_D values are over 6%, as seen in Fig. 3 and Table 1. In fact, the so-called half-reaction time, $t_{0.5}$, which simply corresponds to the reaction time needed to attain $\alpha = 0.5$, decreases markedly with the increase in P_D . Interestingly enough, all samples showed approximately the same maximum in the value of $t_{0.5}$, corresponding to ~ 7 min. This value gives an idea of the fastest possible rate attainable in the reduction of CrO_2 by hydrogen.

The present results show quite clearly the important influence exerted by the porous texture in the reactivity of chromium dioxide towards hydrogen.

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