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KINETICS AND MECHANISTIC ASPECTS OF THE INTERCONVERSION PROCESS $CrO_2 \rightleftharpoons CrOOH$. ISOTOPIC EFFECT

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ABSTRACT

The kinetics and mechanistic aspects concerning with the interconversion process $CrO_2 \rightleftharpoons CrOOH$ have been studied. The oxidation process appears to be governed by an Avrami kinetics equation. However, the back reaction obeys to an onedimensional duffusion kinetics model in which the hydrogen diffuse along the empty tunnels that parallel to the c-axis are present in the rutile-type structure. the isotopic effect concerning with the reduction process have also been studied.

INTRODUCTION

Chromium dioxide is an usefull material because of it's magnetic properties and can be used for magnetic tape applications (1).

It is a metaestable compound which decomposes to α-Cr_2O_3 when is heated in air or under vacuum at temperatures up to 573 K (2). It has also been observed that CrO_2 treated under hydrothermal conditions. reducing atmosphere or even in water at 370 K yields β-CrOOH (3, 4). These results indicate that the interconversion process between both compounds can be expresed according to, $CrO_2 \rightleftharpoons CrOOH$. The facility of this of this process was explained by the close analogy existing between the structure of both compounds; CrO_2 has the tetragonal rutile-type structure, while the β-CrOOHwhich is antiferromagnetic and non-metallic shows a structure which can be described as an orthorhombic distortion of the rutile structure. For this reason this reaction has been considered as topotatic (5).

More recently it has been shown that the reduction of CrO_2 to give CrOOH happens by means of a direct interstitial mechanism in which the hydrogen diffuses along the empty tunnels which are present in the structure of CrO_2 (6). It has also been observed, that this reaction is very much influenced by the presence of extended defects and the porous texture formed during the preheating treatment at the reduction temperature (7).

We report in this paper the study of the reduction of CrO_2

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with deuterium and the kinetics and mechanistic asnects concerning with the oxidation process of CrOOH to CrO_2.

EXPERIMENTAL

Samples of CrO_2 and CrOOH were supplied by the R.C.A laboratories, and they are formed by prismatic particles with an average lenght of 0.362 μm.

Magnetic susceptibility measurements were performed in a Faraday apparatus described elsewhere.

Infrared spectroscopy study was made in a 325 Perking Elmer Spectrophotometer and the sample was prepared by pressing it with powdered KBr to form a disk.

The characterization of the samples by means of X-ray diffraction was performed in a Siemens D-500 diffractometer with CuK_α radiation.

Reduction and oxidation experiments were performed on a thermogravimetric apparatus based in a Cahn electrobalance and a Dupont equipment respectively. Full details of these experimental procedures have been given earlier (6, 7).

RESULTS AND DISCUSSION

1. Oxidation of CrOOH to CrO_2 in air

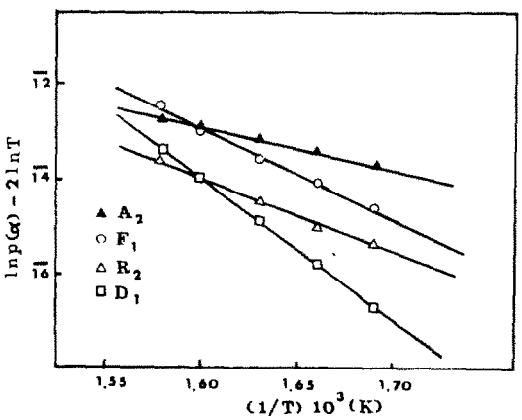

Figure 1.- Representation of the TG data according to Redfern and Coats method (8).

The TG diagram obtained in the decomposition of CrOOH to CrO_2 in air has been analyzed by means of the integral Coats and Redfern method (8). This procedure permits to calculate the activaction energy, E_A and the preexponential factor, A. However, our results can be fitted to at least four different gas-solid kinetics models (9), as shown in Figure 1.

On the other hand, the analysis of the oxidation isotherms, obtained in air

at different temperatures ranging between 579 K and 608 K, indicates that the kinetics of the process correspond to a bidimensional Avrami model In agreement with this model the kinetics of this can be explained by the formation of nuclei of CrO_2 on the surface of the CrOOH and its subsequent growing in two directions. At the final stages of the reaction a decrease in the reaction rate is observed as consequence of the over laping of these nuclei.

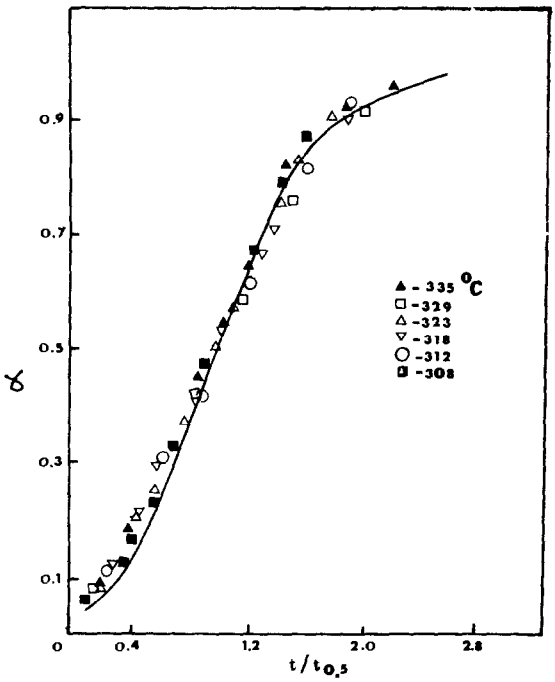

Figure 2.- Reduced time plot obtained in the isothermal decomposition of CrOOH. Full line is the representation of the bidimensional Avrami equation.

2. Reduction of CrO_2 with Deuterium. Isotopic effect

The reduction deuterium isotherms, obtained at different temperatures, show the same features than those obtained in a previous work with hydrogen (6). As in the case of the hydrogenation reaction the rate increases with the temperature, the final reduction stages are not fully reduced and the magnetic susceptibility measurements permit to detect the presence of some CrO_2 in these products.

The diffusion coeficient values are of the order of 10^{-14} cm^2s^{-1} and those corresponding to the hydrogen are higher than those obtained with deuterium. These results reveal the existence of the isotopic effect as consequence of the smaller mass of the former. However, the D_H/D_D ratio increases with the decreasing temperatures taking the classical ratio value of $\sqrt{2}$ only about 513 K.

The plot of log D_H/D_D vs. the reciprocal temperature, fits a straigh line which could correspond to an Ebisuzaki et al. equation (10), for which $\Delta E < 0$, being $\Delta E = E_H - E_D$, as can be seen in Figure 3.

The increase of the D_H/D_D ratio at low temperatures can be attribute to a tunnel effect, that at these low temperatures become important and promotes the diffusion of hydrogen as compared to the deuterium.

Although, it has been demonstrated the existence of the isotopic effect, the results can not be fully explained, because the system studied appears to be very complex. In this sense, the diffusion process implies a chemical reaction giving rise to a structural changes in the solid and no theoretical model has yet been proposed.

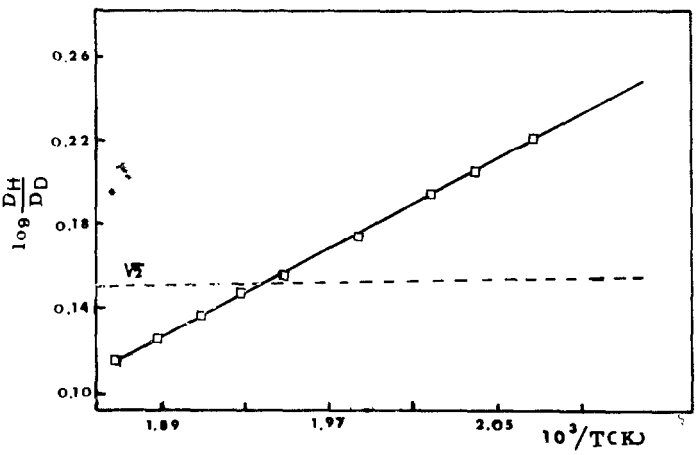

Figure 3.- Representation of the log D_H/D_D ratio vs. the reciprocal temperature for the reduction of CrO_2. Dotted line is the classical D_H/D_D ratio.

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