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LIMITATIONS IN THE FORMAL KINETIC ANALYSIS OF ISOTHERMAL AND THERMOGRAVIMETRIC DATA

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ABSTRACT

The kinetics of the dehydroxilation process under vacuum of three selected oxyhydroxides (γ-MnOOH, γ-FeOOH and CoOOH) are studied. The usual criterion used in the selection of the true rate law, based on the highest value of the linear regression coefficient in the plots obtained from analysis of isothermal and TG traces and the Arrhenius equation proves inadequate when statistical tests are performed. The comparison of activation energy values calculated from isothermal and TG data analysis provides additional information, although the ambiguity cannot be overcome.

INTRODUCTION

The products of the thermal decomposition of CoOOH and γ-FeOOH are known to be independent of the atmosphere in which they are developed although the stoichiometry differs in each case. On the other hand, the dehydration product of γ-MnOOH has been identified as MnO_2 in oxygen atmosphere and a mixture of Mn_3O_4 and Mn_5O_8 in vacuum (ref.1). A recent report in this respect revealed the occurence of γ-Mn_2O_3 in samples of decomposed γ-MnOOH prior to oxide disproportionation (ref.2).

Apart from these divergences, some doubts regarding the kinetics of these decomposition reactions arise upon analysis of thermogravimetric and isothermal weight loss data. Thus, the decomposition of CoOOH has been previously studied (ref.3 and 4) but the final identification of the true mechanism requires the use of other techniques such as X-ray diffraction and electron microscopy. Similarly, Giovanoli and Brutsch (ref. 5) have studied the kinetics of the thermal decomposition of γ-FeOOH, but the reported data should be interpreted with caution as shown below.

The results discussed in this paper show the limitations common to the formal kinetic analysis of these reactions from weight loss data, and which may be extended to other dehydroxylation processes.

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METHODS

Samples of γ-MnOOH, γ-FeOOH and CoOOH were synthetized according to the methods in ref. 1, 5 and 6, respectively.

Isothermal and thermogravimetric data were obtained with a Cahn electrobalance RG model under dynamic vacuum (ca. 10^{-3} Torr) at different temperatures and heating rates. The data were analysed by applying nine kinetic models which included processes governed by growth of nuclei (A_2 and A_3), surface nucleation followed by the movement of the resulting interface (R_2 and R_3), transport phenomena (D_1, D_2, D_3 and D_4) and first order reaction (F_1).

RESULTS AND DISCUSSION

The isothermal (α,t) measurements for CoOOH, γ-FeOOH and γ-MnOOH were recorded in the temperature range 236-268, 197-229 and 174-227°C respectively. In all cases α reached an asymptotic value at the lowest temperature. The nine kinetic ~~functions~~ considered in the analysis were plotted against time in order to obtain the rate constants and linear regression coefficients at each temperature. The plots showed poor linearity, especially at low temperatures. Direct comparison of correlation coefficients indicates that a different mechanism might describe the reactions at the various temperatures. Moreover, if the statistical t test is carried out, the regression coefficients yield no significant differences between kinetic laws in most cases. Thus, the analysis makes it impossible to select a single mechanism on the basis of r coefficients. However, in the first instance it is possible to eliminate certain kinetic laws, such as the diffusion laws, in decomposition at high temperatures. It should be noted that the statistical F test should not be used in this type of analysis since the dependence of the kinetic functions of α is proved by the significant values of r between laws. The limitations mentioned above extend to the use of reduced time plots or the alternative method suggested in ref.7.

An additional uncertainty in these data may be observed in the light of the Arrhenius plots. For each oxyhydroxide, activation energy values are very close regardless of the kinetic law used in the calculation. The mean activation energies and standard deviations calculated by this procedure were 193±4, 103±4 and 125±12 KJmol^{-1} for CoOOH, FeOOH and MnOOH, respectively. The similarity between the activation energies of manganite and lepidocrocite and the high value obtained for CoOOH could be related to the presence of an electron transfer process during the decomposition of the latter compound, which is absent during the formation of γ-Fe_2O_3 and γ-Mn_2O_3.

The TG curves of the three compounds were analysed by the Coats and Redfern method (ref.8). By applying a similar statistical method to that carried out in the isothermal kinetic analysis the regression coefficients cannot be used to select the best linearity. A summary of the final results, with reference to TG traces recorded at 2°Cmin^{-1}, is included in Table 1. In these studies, the heating rate has been found to be an important factor since the values of Ea decrease as the heating rate increases. Our results agree with the conclusions in ref.9 and corroborate the idea that a better thermal equilibrium is reached and dynamic data come close to isothermal measurements when low heating rates are chosen.

TABLE 1

Results of the analysis of TG traces at a heating rate of 2°min^{-1} by the Coats and Redfern approach. Activation energies are expressed in KJmol^{-1}.

	CoOOH		γ-FeOOH		γ-MnOOH	
Rate law	r	Ea	r	Ea	r	Ea
F_1	-0.9959	171	-0.9965	204	-0.9994	103
A_2	-0.9952	81	-0.9962	98	-0.9994	48
A_3	-0.9947	51	-0.9960	63	-0.9991	29
R_2	-0.9910	143	-0.9860	166	-0.9972	86
R_3	-0.9931	151	-0.9903	178	-0.9983	91
D_1	-0.9821	249	-0.9710	284	-0.9902	151
D_2	-0.9884	277	-0.9809	317	-0.9950	168
D_3	-0.9936	313	-0.9908	363	-0.9981	190
D_4	-0.9905	289	-0.9847	332	-0.9960	175

If the activation energy values in Table 1 are compared with those obtained under isothermal conditions - see above - some models can be discarded as operative mechanisms for the dehydration processes. On the basis of this assumption, a first order expression seems to be obeyed by γ-MnOOH and CoOOH while the expression referred to as the Avrami-Erofeev mechanism (A_2) is found to describe the decomposition of lepidocrocite.

These conclusions are difficult to justify in the light of the structure, particle texture and morphology and stoichiometry of the final product. Thus, manganite and lepidocrocite are isostructural, the particles of both reactants and decomposition products have similar lath morphology as shown by electron microscopy, and an analogous porous system is developed during the dehydration process. These data should be consistent with a similar decomposition mechanism.

On the other hand, the CoOOH/Co_3O_4 system differs considerably. Apart from water loss, the reaction proceeds via the release of oxygen which involves an electron transfer phenomenon. Moreover, both phases show a platelike morphology, and the decomposion leads to cracks on the surface instead of a porous system. These observations have been interpreted in terms of a random nucleation process, F_1 (ref.4).

The results reported here, however, do not concur with the classification proposed in ref.10, in which pore analysis is used to ascertain the actual mechanism of the reaction.

In the light of the above considerations, it may be stated that analysis of weight loss data is insufficient for determining the mechanism of a dehydroxilation process such as those considered in this paper, or, in our opinion, others reported elsewhere such as CrOOH, caolinite, etc. Attention should be drawn to the application of additional techniques that provide structural information to support the interpretation of kinetic measurements.

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