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Synthesis of acicular hematite catalysts with tailored porosity

L.A. Pérez-Maqueda[a], J.M. Criado[a], J. Subrt[b] and C. Real[a]

[a] *Instituto de Ciencias de Materiales de Sevilla, Centro Mixto Universidad de Sevilla-C.S.I.C., c/Américo Vespucio s/n, Isla de La Cartuja, 41092 Sevilla, Spain*

[b] *Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 25068 Rez, Czech Republic*

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The topotactic thermal decomposition of a synthetic acicular goethite sample into hematite has been studied by controlled rate thermal analysis (CRTA). This method allows a precise, simultaneous and independent control of both the partial pressure of water vapour generated from the decomposition of goethite and the decomposition rate of this precursor. It has been demonstrated that the CRTA method allows obtaining acicular particles of α-Fe_2O_3 with tailored porosity oriented along the c lattice axis (the longest axis of the particle). This finding would be of great potential interest from the point of view of the use of this material as a catalyst.

Keywords: acicular hematite, porosity, controlled rate thermal analysis (CRTA)

1. Introduction

Hematite (α-Fe_2O_3) is of interest as a catalyst [1–3]. Thus, hematite promoted with K_2O or MoO_3 shows a high catalytic activity for the dehydrogenation of ethylbenzene to styrene, the vapour-phase oxidation of alcohols to aldehydes and ketones, and the large-scale manufacture of butadiene to produce elastomers [3]. Catalysts marketed with the trade name Nanocat used as burning-rate catalyst for solid fuels consist of a mixture of nanophased two-line ferrihydrite with hematite [4–6]. Brown et al. [1] have shown in a recent paper that the sulfation of the iron oxide obtained from goethite or ferrihydrite precursors enhances its catalytic selectivity towards the methane oxidation to methanol with regards to the total oxidation of the hydrocarbon.

The above catalysts are used as finely divided powders or as porous solids with a high ratio of surface area to volume. Thus, the synthesis of iron oxides with tailored porosity is a matter of great interest. The thermal decomposition of goethite (α-FeOOH) according to the reaction

$$2\alpha\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3 + \text{H}_2\text{O} \qquad (1)$$

could be a proper way for synthesising hematite catalysts with controlled porosity. Naono et al. [7,8] have shown that lath-like goethite crystals undergo a topotactic dehydroxylation, where the original single crystals of goethite are replaced by a highly ordered aggregate of small α-Fe_2O_3 crystals with a large amount of pores. Many studies have been devoted to the elucidation of the formation of pores during the dehydroxylation of pure and substituted goethite [9–12]. The effect of several experimental parameters, such as annealing temperature or atmosphere on the porosity has been studied. However, it must be pointed out that the calcination of goethite has been carried out under isothermal conditions or under a linear heating program until reaching the final annealing temperature. None of these two procedures allows discerning the influence of the decomposition rate of goethite from the influence of the partial pressure of the water vapour generated on the porosity of hematite obtained as the final product.

In this work, the constant rate thermal analysis (CRTA) method has been used for monitoring the thermal decomposition of goethite. The CRTA method has been previously used for controlling the texture and structure of some materials through the kinetic control of the thermal decomposition of their corresponding precursors [13–16]. The results here reported constitute the first attempt of using the CRTA method for controlling the texture and structure of the final products obtained from the thermal decomposition of goethite.

2. Experimental

2.1. Preparation of goethite sample

The preparation procedure consisted of the following steps: (i) A solution containing 250 $\mathrm{g\,l^{-1}}$ of $FeSO_4{\cdot}7H_2O$ was neutralised at room temperature with a 13.5 wt% NH_4OH solution until 25% of the iron ion was precipitated. (ii) Air was bubbled through the dispersion until the pH of the dispersion dropped to appoximately 4 and the colour turned from dark blue to yellow. (iii) The temperature was elevated to 60 °C and the pH value was maintained in the range 3.5–4 until the Fe disappeared from the solution. (iv) The yellow precipitate was then separated by filtration and washed with distilled water until no SO_4^{2-} was detected in the filtrate. (v) Finally, the solid was dried at room temperature overnight.

2.2. Methods

Crystalline structures of the solids were studied by powder X-ray diffraction (XRD) with Cu Kα radiation and a graphite monochromator (model PW 1060, Philips). The transmission electron microscopy (TEM) analysis was performed with a Philips CM 200 microscope working at 200 kV. The specific surface area was measured by the BET method (model 2200, Micromeritics) with nitrogen gas at 78 K.

To study the thermal transformation of the goethite samples into hematite, some experiments were carried out using a linear heating rate program both in vacuum and static air. Another experiment was performed in a closed tube under the pressure of water vapour originated in the decomposition.

In addition, a controlled rate thermal analysis (CRTA) equipment developed in our laboratory has been used to study this thermal transformation. The instrument consists of a tubular furnace Carbolite MTF 12/25B, that can be operated up to 1200 °C, and it has been connected to a conventional high-vacuum system that allows pressures down to 2×10^{-6} mbar. The pressure gauge output is connected by an interface to the temperature controller of the furnace in a similar way as described by Rouquerol [13,16–19]. Thus, the gas pressure around the sample (P) is kept constant in a selected value. The gas pressure can be controlled in a range from 10^{-5} to 10 Torr. Since the gas pressure of the gases generated in the reaction is proportional to the reaction rate (C), the reaction rate is also kept constant during the whole dehydroxylation process. This CRTA instrument allows the change of the reaction rate while keeping the water vapour pressure constant by modifying the amount of sample or the pumping rate.

3. Results and discussion

Figure 1(a) illustrates the transmission electron micrographs of the goethite sample prepared under the conditions described above. This sample is constituted by acicular particles having a specific surface area, as calculated by the single-point BET method, of 43 $\mathrm{m}^2\,\mathrm{g}^{-1}$. The X-ray diffraction (XRD) pattern (figure 2(a)) of this solid is characteristic of α-FeOOH. Figure 3 shows the thermogravimetric curve in vacuum at 20 °C min^{-1} heating rate of the goethite sample previously treated at 110 °C for 1 h to remove the hydration water. The weight loss over the range 200–350 °C was 10% which corresponds to the dehydroxylation of FeOOH according to equation (1). The final product of the thermal decomposition of goethite on heating at 350 °C was pure hematite, as illustrated by the XRD pattern of the goethite sample after calcination at 350 °C for 1 h in vacuum (figure 2(b)).

To study the texture and structure of the products obtained from the thermal decomposition of goethite, some experiments were carried out using a linear heating program under different conditions. The values of the specific surface area for the resulting α-$\mathrm{Fe_2O_3}$ samples are given in table 1. In all these experiments, temperature was increased up to 350 °C and maintained at this value for 1 h. The TEM micrographs of the hematite particles are shown in figure 1. The size and shape of the precursor seem to be maintained as expected for a topotactic reaction [7,20,21], while a large number of pores have been generated. The solids with higher specific surface present slit-shaped pores along the longest direction of the particles (figure 1(b)). It has been reported from electron diffraction data of acicular microcrystals of α-$\mathrm{Fe_2O_3}$ that the elongated direction of the microcrystal is perpendicular to the c axis [22]. Thus, the slit-shaped pores are opened along an axis perpendicular to c. The samples with lower specific surface area have randomly distributed isolated circular pores (figure 1(d)). A similar relation between specific surface area and porosity for hematite obtained from the thermal decomposition of goethite has been described elsewhere [7].

The effect of the heating rate on the porosity is different for the experiments carried out in vacuum and in static air. Thus, in vacuum an increase in the heating rate produces an increase in the specific surface area, whereas in static air the effect is just the opposite. This behaviour perhaps could be explained by considering that the developed porosity depends on both the decomposition rate of the precursor and the partial pressure exerted in the close vicinity of the sample by the water vapour self-generated in the reaction. These two factors would depend on the heating rate and the atmosphere surrounding the sample at the beginning of the experiment. Therefore, it would be interesting to carry out a careful independent analysis of the influence of the decomposition rate and the partial pressure of water vapour on the texture of α-$\mathrm{Fe_2O_3}$ obtained from the thermal decomposition of goethite. The controlled rate thermal analysis (CRTA) is a suitable method for this purpose.

The CRTA method allows discerning the influence of both the reaction rate and the partial pressure of water vapour on the texture and structure of the iron oxide obtained. Experiments were performed in the instrument described in section 2. As an example, the plot of both temperature and partial pressure of water vapour recorded as a function of the time for the decomposition of the goethite sample by CRTA under a constant pressure $P = 5.5 \times 10^{-5}$ mbar and a decomposition rate $C = 6.5 \times 10^{-4}\ \mathrm{min}^{-1}$ is shown in figure 4. This figure illustrates how the temperature changes in such a way that the reaction rate is kept constant during all the decomposition process. Figure 5(A) includes the reacted fraction (α) values as calculated from the integer of the pressure curve between the initial and actual point and divided by the total area as a function of the temperature (T) for three experiments carried out at different decomposition rates. The α–T plots obtained for two CRTA experiments performed at the same reaction rate but at different partial pressures are included in figure 5(B). These two latter plots (figure 5) illustrate how the temperature ranges at which the decomposition takes place depend on the conditions selected by

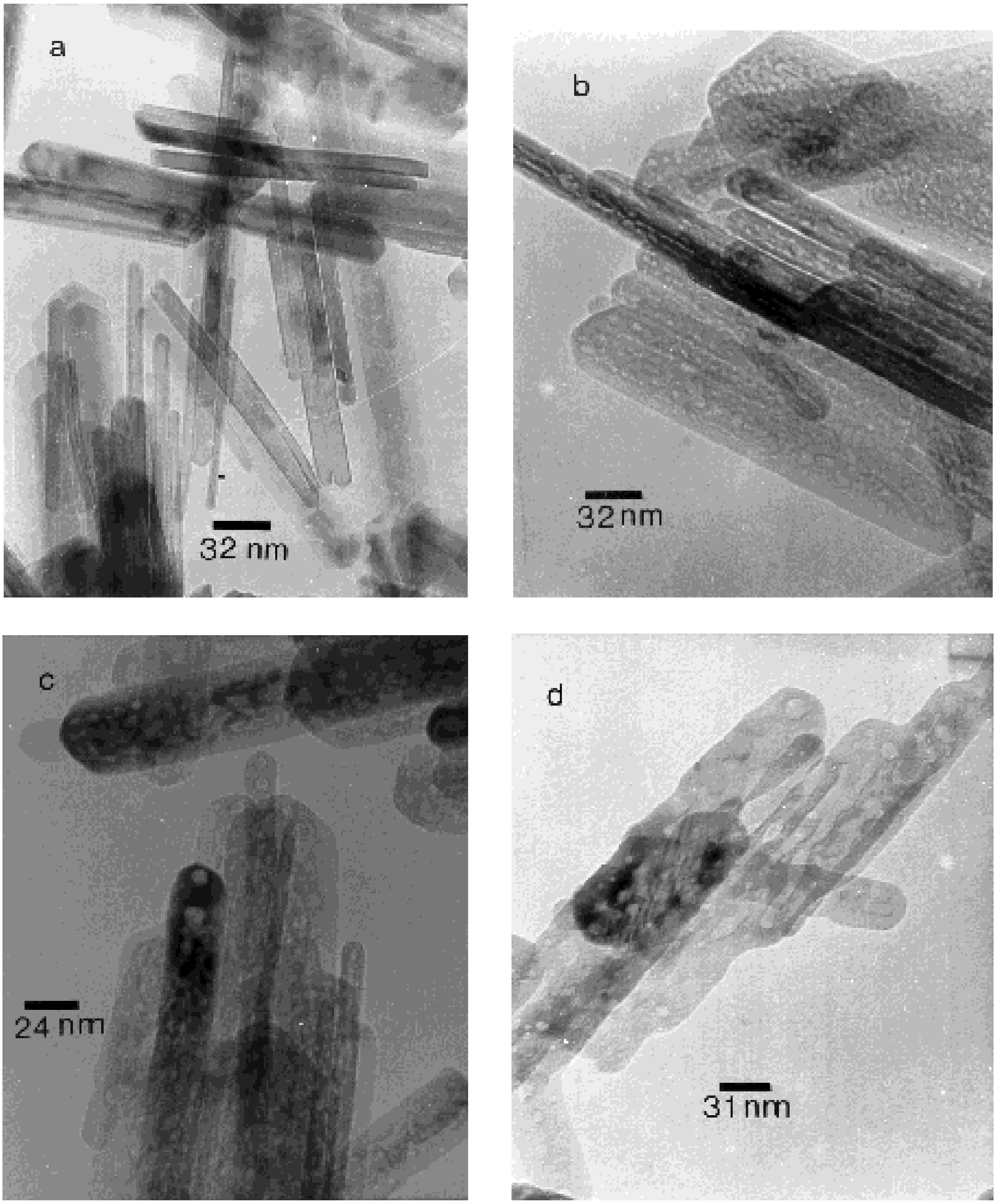

Figure 1. TEM micrographs of: (a) original goethite sample; (b) goethite sample decomposed in open air at 0.5 °C min^{-1}; (c) goethite sample decomposed in open air at 20 °C min^{-1}; and (d) goethite sample decomposed inside a closed tube.

the user. Differences in the temperature ranges of decomposition are in some cases of more than 50 °C. For the experiments carried out at the same water vapour pressure, the lower decomposition rate, the lower temperature range of the reaction. This latter behaviour has been explained taking into consideration the solid state kinetic equations in a previous publication [23].

The decomposition of goethite by CRTA under the above conditions was over before 300 °C. However, on completion of the reaction, the temperature of the sample was increased up to 350 °C and annealed for 1 h under high vacuum before cooling down. This normalised thermal treatment would ensure that the differences observed in texture and morphology of the hematite are due to the experimental

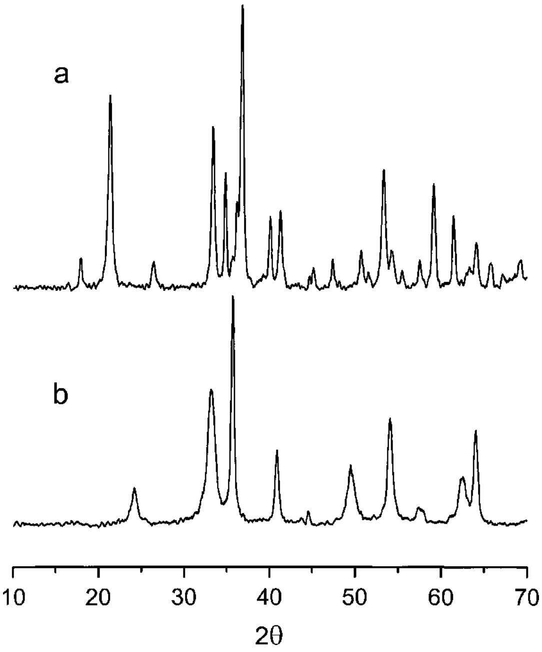

Figure 2. Powder X-ray diffraction (XRD) patterns of (a) goethite sample and (b) goethite sample calcined in vacuum at 350 °C for 1 h.

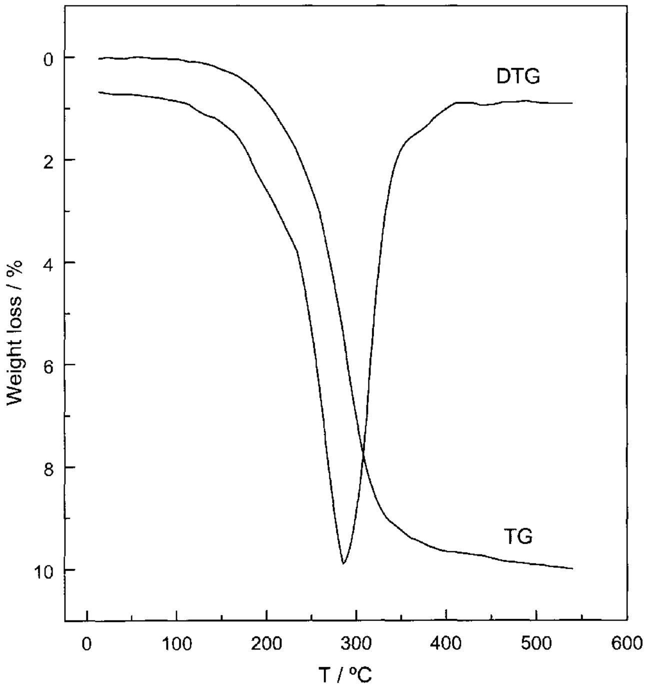

Figure 3. Thermogravimetric curve in vacuum at a heating rate of 20 °C min^{-1} of the goethite sample, previously treated at 110 °C for 1 h to remove the hydration water.

conditions used for decomposing the precursor rather than to the highest temperature of the treatment.

It can be noted the low-temperature range at which takes place the goethite dehydroxylation under a constant pressure of 5.5×10^{-5} mbar and at $C = 1.8 \times 10^{-4}$ min^{-1} (figure 5(A)) as compared to the values obtained at a constant heating rate $\beta = 20$ °C min^{-1} (figure 3). This behaviour is related to the different experimental conditions used. The dehydroxylation rate and the partial pressure of the water vapour generated in the neighbourhood of the sample must be considerably larger in the latter case.

Table 1

Specific surface areas of the hematite samples prepared by decomposition of the goethite sample at linear heating rate under different atmospheres and linear heating rate.

Atmosphere	Heating rate (°C min^{-1})	Specific surface area (m^2 g^{-1})	Figure
Vacuum	0.5	83	
	20	101	
Open air	0.5	101	1(b)
	20	77	1(c)
	∞^a	56	
Closed tube	∞^b	49	1(d)

[a] The sample was introduced directly into the furnace at 350 °C.

[b] The sample was introduced into a closed tube, so the water pressure over it was during the dehydroxylation ∼8 × 10^3 Torr.

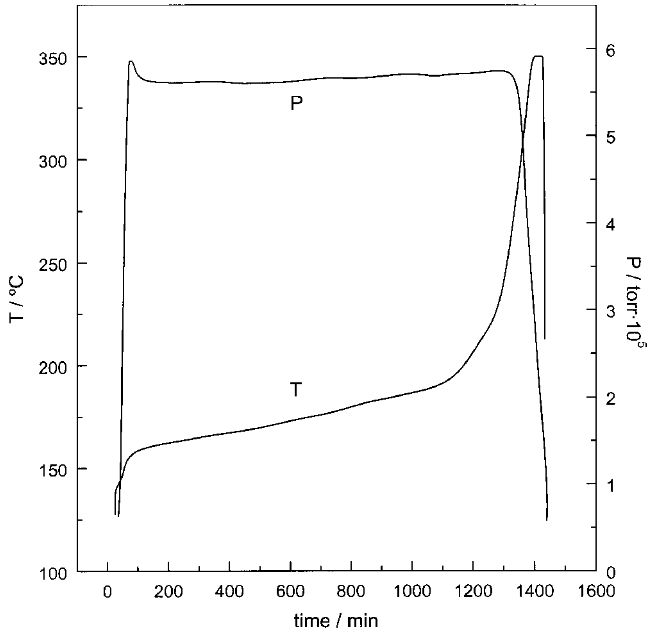

Figure 4. The plot of the evolution of the temperature and partial pressure of water vapor recorded as a function of time for the decomposition of the goethite sample by CRTA under a constant pressure $P = 5.5 \times 10^{-5}$ mbar and a decomposition rate $C = 6.5 \times 10^{-4}$ min^{-1}.

Table 2 shows the specific surface areas of hematite samples obtained by using the CRTA method for decomposing the α-FeOOH. These samples (figure 6) present similar relationships between specific surface area and porosity to the ones obtained from the thermal decomposition of goethite under a linear heating rate program (figure 1). Additionally, table 2 shows that the higher the water vapour pressures on the goethite samples, the lower the specific surface areas of the resulting oxides. On the other hand, the specific surface area is also influenced by the decomposition rate. The decrease in the specific surface on hematite by increasing either the reaction rate or the partial pressure of water

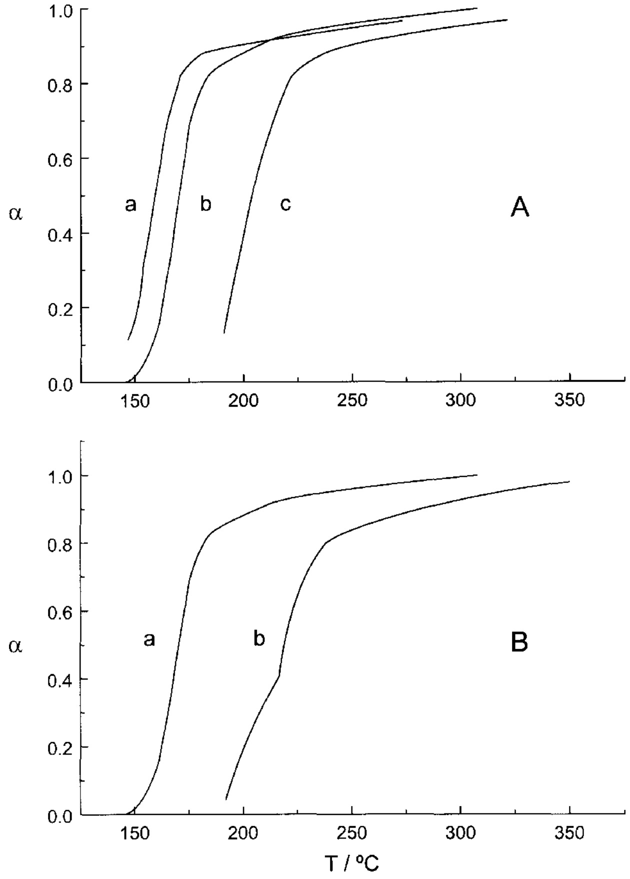

Figure 5. Reacted fraction (α) as a function of temperature (T) for CRTA experiments carried out (A) at the same pressure, 5.5×10^{-5} Torr, and three different reaction rates: (a) 1.8×10^{-4}, (b) 6.5×10^{-4}, and (c) 3.3×10^{-3} min^{-1}; and (B) at the same reaction rate, 7.0×10^{-4} min^{-1}, and two different control pressures: (a) 5.5×10^{-5} and (b) 3.7 Torr.

Table 2

Specific surface areas and crystallite sizes for the hematite samples prepared by decomposition of the goethite sample by CRTA at different control pressures and reaction rates.

Control pressure (Torr)	Reaction rate (min^{-1})	Specific surface ($\text{m}^2\,\text{g}^{-1}$)	Figure
5.5×10^{-5}	3.3×10^{-3}	102	6(a)
	6.5×10^{-4}	89	
	2.2×10^{-4}	76	
	1.8×10^{-4}	45	
3.7	3.0×10^{-3}	83	6(b)
	7.0×10^{-4}	58	
8.2	7.6×10^{-4}	44	6(c)

vapour can be interpreted considering the increase of the decomposition temperature associated with the increase of the selected decomposition rate, C. Under these conditions, the mobility of the surface ions may be promoted resulting in a faster pore growth and elimination.

Finally, considering the results obtained from CRTA, it is possible to understand the apparently confusing results for the texture of hematite obtained from the thermal decomposition of goethite under a linear heating rate. Under

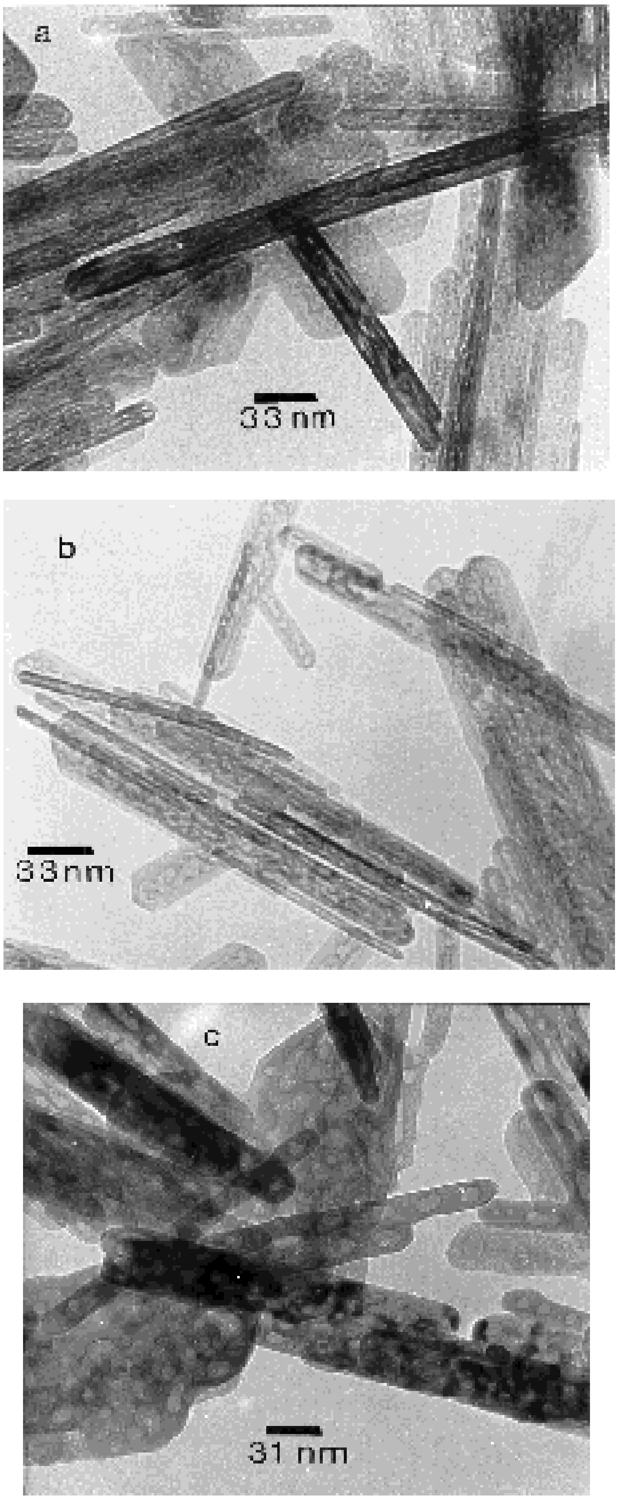

Figure 6. TEM micrographs corresponding to the hematite samples obtained by CRTA under the following experimental conditions: (a) $C = 3.3 \times 10^{-2}$ min^{-1} and $P = 5.5 \times 10^{-5}$ Torr, (b) $C = 3.0 \times 10^{-3}$ min^{-1} and $P = 3.7$ Torr, and (c) $C = 7.57 \times 10^{-4}$ min^{-1} and $P = 8.2$ Torr.

any particular experimental conditions, an increase in the heating rate, because of kinetic reasons, necessarily leads to an increase in the reaction rate. This increase in the reaction rate, according to our CRTA results, should produce an increase in the specific surface area of the resulting hematite products. However, the increase in the heating rate could also produce an increase in the vapour pressure on the proximity of the sample, and consequently a decrease in the specific surface area of the hematite. For the experiments in vacuum, the increase in the reaction rate is the determining parameter, probably because the pumping minimises the influence of the water vapour. Therefore, an increase in the heating rate produces an increase in the specific surface area. On the other hand, for the experiments in static air, the water vapour pressure has a more significant effect, and hence an increase in the heating rate could produce a decrease in the specific surface of hematite. Taking into account that the reaction rate and the partial pressure of water vapour work in opposite directions, it is difficult, if not impossible, to forecast the texture of the final products obtained from the thermal decomposition of the goethite without a precise control of both experimental parameters. It has been shown that the CRTA method outlined here is a proper procedure for overcoming this problem.

4. Conclusions

The controlled rate thermal analysis (CRTA) method has allowed the independent study of the effects of both the dehydration rate (C) of goethite and the water vapour pressure (P) self-generated in the reaction on the porosity of hematite obtained as the final product. Both P and C have a significant influence on the porosity of hematite obtained that cannot be interpreted as a function of the annealing temperature, provided that all the samples here investigated have been annealed at a same final temperature of 350 °C. It has been concluded that slower reaction rates yield more porous materials than faster ones. On the other side, an increase in the water vapour pressure produces a decrease in the porosity.

The method of CRTA here described allows preparing acicular hematite particles with controlled porosity orientated across the long axis of the particles. This feature would be of potential interest for improving the performance of this material for catalytic uses.

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