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The influence of preparation and doping on the reducibility of hematite by hydrogen

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Samples of hematite and of hematite doped with 1 at% lithium and 1 at% vanadium are prepared by the hot kerosene drying technique. The doped samples are also prepared by an impregnation method. The various samples are used to study the reduction with hydrogen to form iron. The results indicate that the rates of reduction are strongly influenced by the particle size of the initial samples and by the repartition of the additive in the bulk and surface layer of the hematite particles. It has been shown that both additives can retard the rate of reduction. The lithium exerts its maximum influence when present in solid solution and vanadium when concentrated in the surface layer. The importance of a careful preparation of samples to be used for reduction studies, is stressed.

1. Introduction

The reduction of hematite (α-Fe_2O_3) to form iron comprises a sequence of successive reactions [1–8]. The intermediate products are magnetite and, in the majority of studies, also wustite. By the direct reduction, using carbon, the Boudouard reaction must also be taken into account.

In several publications it is reported that the rate of reduction of iron oxides is affected by small amounts of various inorganic compounds [1, 7–17]. According to most results the oxides of the alkali and earth-alkaline metals increase the rates of reduction of iron oxides [1, 7, 12, 15] and by direct reduction also that of the Boudouard reaction [14, 17]. In some cases, however, opposite results have been obtained. Under certain conditions Li_2O and MgO may retard the reduction process [8] and a similar effect has been reported for K_2O and CaO [12, 13].

It appears that the influence of the additions depends strongly on the state of the sample prior to reduction. In this connection it can be mentioned that NiO is reported either to accelerate or to retard the rate of reduction depending on the impregnation method used [9]. The influence of SiO_2 on the reduction of wustite [18] and that of Al_2O_3 on the reduction of α-Fe_2O_3 [19] are other examples where the state of the starting material can affect the rate both ways.

It is also apparent that the amount of additive may also be of great importance. For calcium a maximum reduction rate of wustite is observed at 1 at%, above which the rate decreases without attaining a minimum value [1, 12].

This decrease is ascribed to a slagging of the samples. A similar effect has been found in the case of potassium. Al_2O_3, on the other hand, causes a minimum reduction rate of α-Fe_2O_3 at 1.5 wt% [19]. At this percentage the physical strength of the magnetite is a maximum, which corresponds to a minimum in the reducibility. In turn this maximum in physical strength is reported to be accompanied by a maximum in the shrinkage of the sample.

The above suggests that the method of preparation may be an important factor contributing to the effects of the additives. Various methods have been used. In several studies the reduction experiments have been carried out with mixtures of the iron oxide and the additives [8, 14, 17, 19, 10]. In order to homogenize the samples, they are usually subjected to thorough mechanical mixing

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and calcining prior to reduction [8, 14, 19]. Secondly, impregnation [19] and co-precipitation [21] methods have also been used. It is the purpose of this paper to show that the preparation of the samples can strongly influence the measured rates of reduction. This will be illustrated by using hematite, pure or doped with 1 at% of either lithium or vanadium. The former is generally accepted to increase the rate of reduction and the latter is reported to decrease the rate [16].

2. Experimental procedure

2.1. Homogeneous samples

Very finely divided, homogeneously doped oxides were prepared by the hot kerosene drying (HKD) technique, previously described by Reynen *et al.* [22]. A solution of iron (II) sulphate (0.40 mol dm^{-3} of $FeSO_4.7H_2O$, [Merck, G.R. grade]) in distilled water, containing the appropriate amount of additive ($LiNO_3$, [Merck, G.R. grade], $VOSO_4.5H_2O$, [Merck] 0.040 mol dm^{-3}) was dispersed in kerosene (Fluka, purum) containing an emulsion stabilizer (5 wt% Span 85 [Atlas Chemicals]), using a special mixer (Ultra-Turrax, Jankel and Kunkel, W. Germany). The kerosene to solution volume ratio was 1 to 1, the mixing conditions were kept constant for all the samples. The obtained emulsion was added dropwise (2 cm^3 min^{-1}) into a thermostatted kerosene bath (500 cm^3, 180° C) under constant stirring. The drying apparatus was so designed that the evaporated water condensed in its upper part and was continuously removed. The anhydrous salt produced in this way was filtered off from the kerosene, washed two times with diethylether (Merck, p.a.), heated in air for 1 h at 200° C and kept in a dessicator. The oxide was obtained by calcining the sulphate precursor in air at various temperatures.

Pure iron oxides were prepared in the same way, starting with a solution containing iron sulphate only. It was established, by X-ray diffraction, that these samples consisted of pure, well crystallized hematite.

2.2. Impregnated samples

Pure iron oxide powders prepared as above were impregnated with 2 cm^3 of a solution of the desired additive per gram of solid (6.26×10^{-2} mol dm^{-3} of $LiNO_3$ or $VOSO_4.5H_2O$, the same as above); enough distilled water was added in order to obtain a slurry. Each slurry was freeze dried and calcined in air for 2 h at 600° C.

TABLE I Summary of the samples used in the present study

Sample	Additive*	Calcination conditions	
		temperature (°C)	time (h)
Homogeneous samples			
F600-4	no	600	4
F600-8	no	600	8
F600-24	no	600	24
F700-16	no	700†	16
F800-16	no	800†	16
F900-16	no	900†	16
FL600-4	Li	600	4
FL600-16	Li	600	16
FL700-16	Li	700†	16
FV600-4	V	600	4
FV600-7	V	600	7
FV600-24	V	600	24
FV650-16	V	650	16
FV700-16	V	700†	16
Impregnated samples‡			
F600-4L	Li	600	4
F700-16L	Li	700	16
F600-4V	V	600	4
F700-16V	V	700	16

*1 atom % with respect to Fe

†sample tempered at 600° C for 16 h in air, after calcination

‡calcination conditions of the oxide *before* impregnation; final calcination for 2 h at 600° C.

Table I presents the composition, calcination temperature and the time of all the samples prepared for the present study.

2.3. Temperature programmed reduction (TPR)

TPR experiments were performed following a method described previously by Robertson *et al.* [23] and already used for the characterization of supported oxides [24]. About 5 mg of iron oxide was placed into a quartz reactor through which the reducing gas (5 vol% hydrogen in argon [Air Liquide]) was flowing at a constant rate (35 cm^3 min^{-1}). Traces of oxygen and water were removed from the gas mixture by means of two columns packed with a 5% Pt/Al_2O_3 catalyst and molecular sieve (5 A° X; Merck) respectively. By means of a tubular furnace, the temperature of the reactor could be increased linearly (10° C min^{-1}) from the ambient temperature up to 900° C.

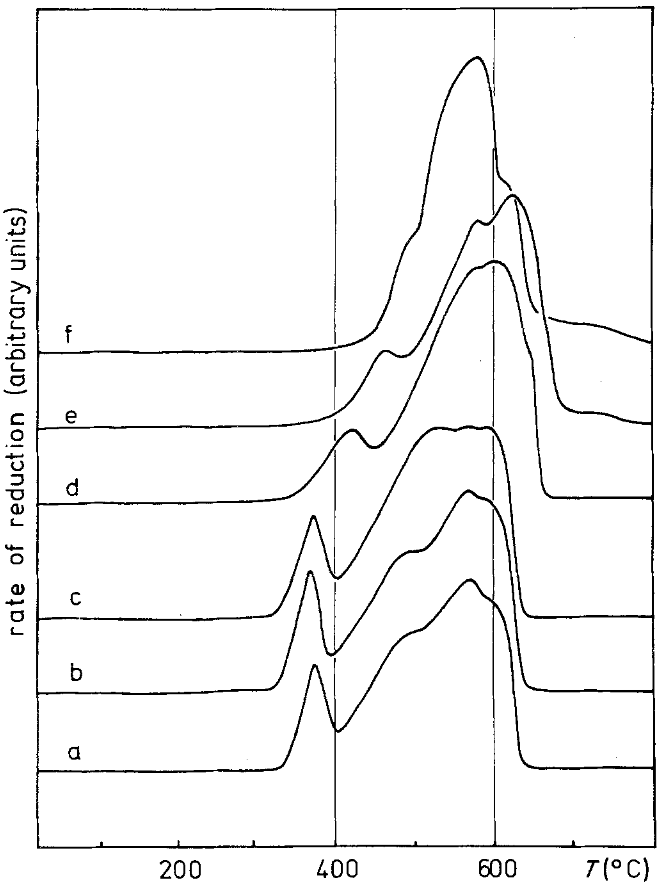

Figure 1 TPR patterns of the pure hematite samples, (a) F600-4, (b) F600-8, (c) F600-24, (d) F700-16, (e) F800-16 and (f) F900-16.

The outlet gas from the reactor was dried in a cold trap (−90° C, liquid–solid methanol mixture) and the hydrogen concentration was followed by means of a thermal conductivity detector. The signal of the detector was proportional to the decrease in hydrogen concentration and served consequently as a measure of the rate of reduction of the sample. This signal, together with that of the chromel–alumel thermocouple, placed in close contact with the sample in the reactor, was taken to a $X-Y$ recorder.

2.4. X-ray diffraction analysis

X-ray powder analysis was carried out in a standard Philips Norelco X-ray diffractometer using the CuKα radiation (Ni filter). The pulse height discrimination of the scintillation counter was set so as to eliminate the fluorescence background coming from the iron.

2.5. Electron microscopy

The samples were dispersed in water using an ultrasonic vibrator and deposited on carbon films supported on standard copper grids for transmission electron microscopy. These specimens were studied both in transmission (TEM) and scanning electron microscopy (SEM) in a Jeol TEMSCAM 100 CX microscope equipped with a Kevex energy dispersive spectrometer for X-ray microanalysis. No additional coating appeared necessary for SEM work.

3. Results

3.1. Temperature programmed reduction

Fig. 1 presents the patterns of the pure hematite samples after various calcination treatments (the F series of samples in Table I). The following features of the curves may be noticed.

Two main reduction steps are apparent for the samples calcined at 600 to 700° C (Curves a, b, c and d). The first peak corresponds to the transition of hematite to magnetite. This has been verified from the X-ray analysis of the intermediate product after the first step of Sample F600-4. Furthermore, it is also in agreement with the ratio 1:9 of the surface areas of the two peaks.

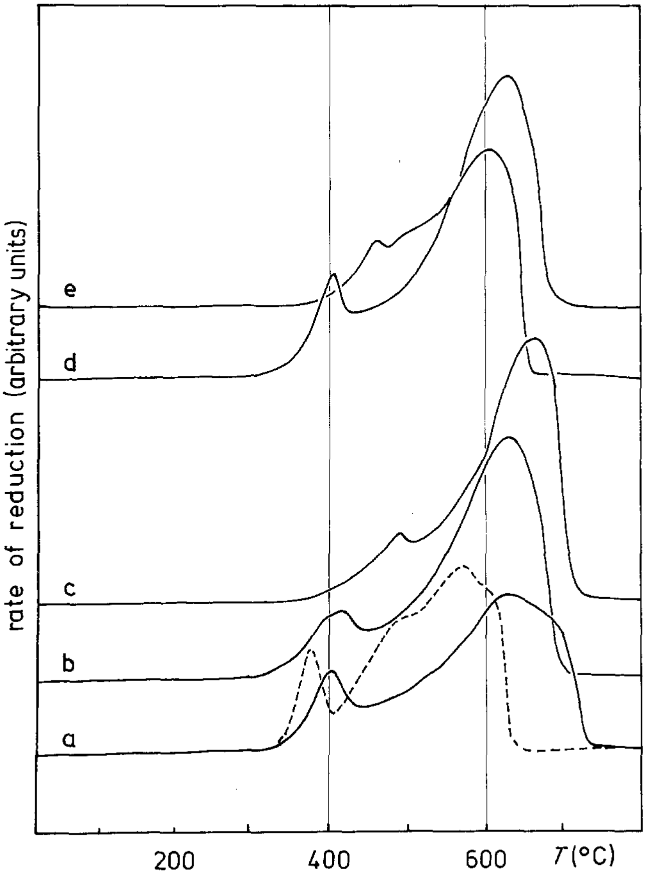

Figure 2 TPR patterns of Li doped hematite samples. (a) FL600-4, (b) FL600-16, (c) FL700-16, (d) F600-4L and (e) F700-16L. The dotted line corresponds to sample F600-4.

A second feature of the TPR patterns in Fig. 1 is that the first reduction peak shifts from about 380° C to higher temperature as the calcination temperature increases, and ultimately merges into the high temperature peak.

Concerning the second peak it may be noticed that its structure is rather sensitive to the calcination time at 600° C; a shoulder, at about 500° C, emerges progressively as the calcination time increases. There is also a tendency of the peak temperature to increase (610 to 620° C) with increasing calcination temperatures.

Fig. 2 shows the TPR patterns of the samples doped with 1 at% Li. The Curves a, b and c correspond to the homogeneous samples and d and e to the impregnated samples. It is apparent that the reduction proceeds through two steps as for the pure iron oxide. Another similarity is the shift of the first reduction peak towards higher temperatures as the calcination time or temperature are increased. The main difference between the patterns in Figs 1 and 2 is that, in the latter, the reduction peaks, for samples calcined at the same temperature are displaced to higher temperatures. Furthermore, it is clear that this displacement is less important for the impregnated samples than for the homogeneous ones.

Fig. 3 presents the TPR-patterns of the samples doped with vanadium. Like before, the samples calcined at the lowest temperature and for the shortest times exhibit two distinct reduction peaks; the low temperature peak appears at the same or slightly higher temperature compared with the corresponding pure sample. The same trends as before are observed when the calcination temperature increases. The impregnated and homogeneous samples calcined at 600° C (Curves a and f) are very similar. There is, however, a marked difference between the patterns corresponding to the two samples calcined at 700° C (Curves e and g). In both, the first reduction peak is hardly noticeable but the reduction takes place at a much higher temperature for the homogeneous sample.

3.2. Electron-microscopy

All samples appeared homogeneous, no separate

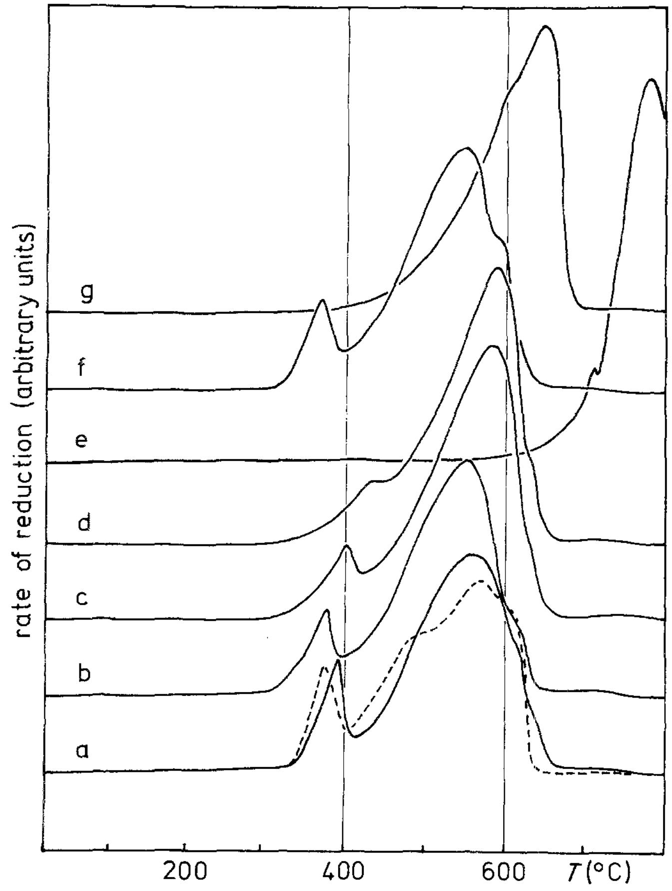

Figure 3 TPR patterns of V doped hematite samples. (a) FV600-4, (b) FV600-7, (c) FV600-24, (d) FV650-16, (e) FV700-16, (f) F600-4V and (g) F700-16V. The dotted line corresponds to sample F600-4.

Li or V bearing phase being observed. Lithium could not be measured by X-ray micro-analysis. No significant divergence from homogeneity could be observed in the repartition of vanadium.

Fig. 4 presents typical SEM-pictures of some samples. In Fig. 5 are shown the ranges of the particle sizes measured on the micrographs for various samples. These ranges are given as twice the standard deviation of the measured distribution of sizes.

No significant difference was found between all the samples prepared at 600° C, whatever the nature of the additive (Li or V) and the way of preparation (HKD or impregnation). The small crystallites (about 50 nm diameter) are agglomerated into very porous spherical aggregates (Fig. 4a). The later originates probably from the kerosene emulsion used for the preparation of the oxides.

After calcination at 700° C, both samples F700-6 and FL700-16 exhibit a sintering of the crystallites into particles about four times larger (see Fig. 4b). As shown in Fig. 4d, the presence of vanadium dramatically increases the sintering at this temperature. The average particle size of vanadium doped samples calcined at 700° C are even about twice as large as the sizes observed for pure samples calcined at 900° C (compare Fig. 4c and 4d). Both impregnated samples F700-16L and F700-16V show particle sizes somewhat larger than F700-16, but considerably smaller than FV700-16.

From the samples F600-4, FL600-4 and FV600-4, micrographs have been taken after temperature programmed reduction to iron (see Fig. 6). The pictures obtained from F600-4 and FL600-4 were very similar (Fig. 6a) except for the fact that the iron particles obtained from FL600-4 were slightly larger. The shapes of the reduced particles obtained from FV600-4 were, however, quite different (Fig. 6b).

4. Discussion

The results show quite clearly that various factors, some of which were not properly understood in the past, can affect the reducibility of hematite, namely: the particle size, the nature of the addi-

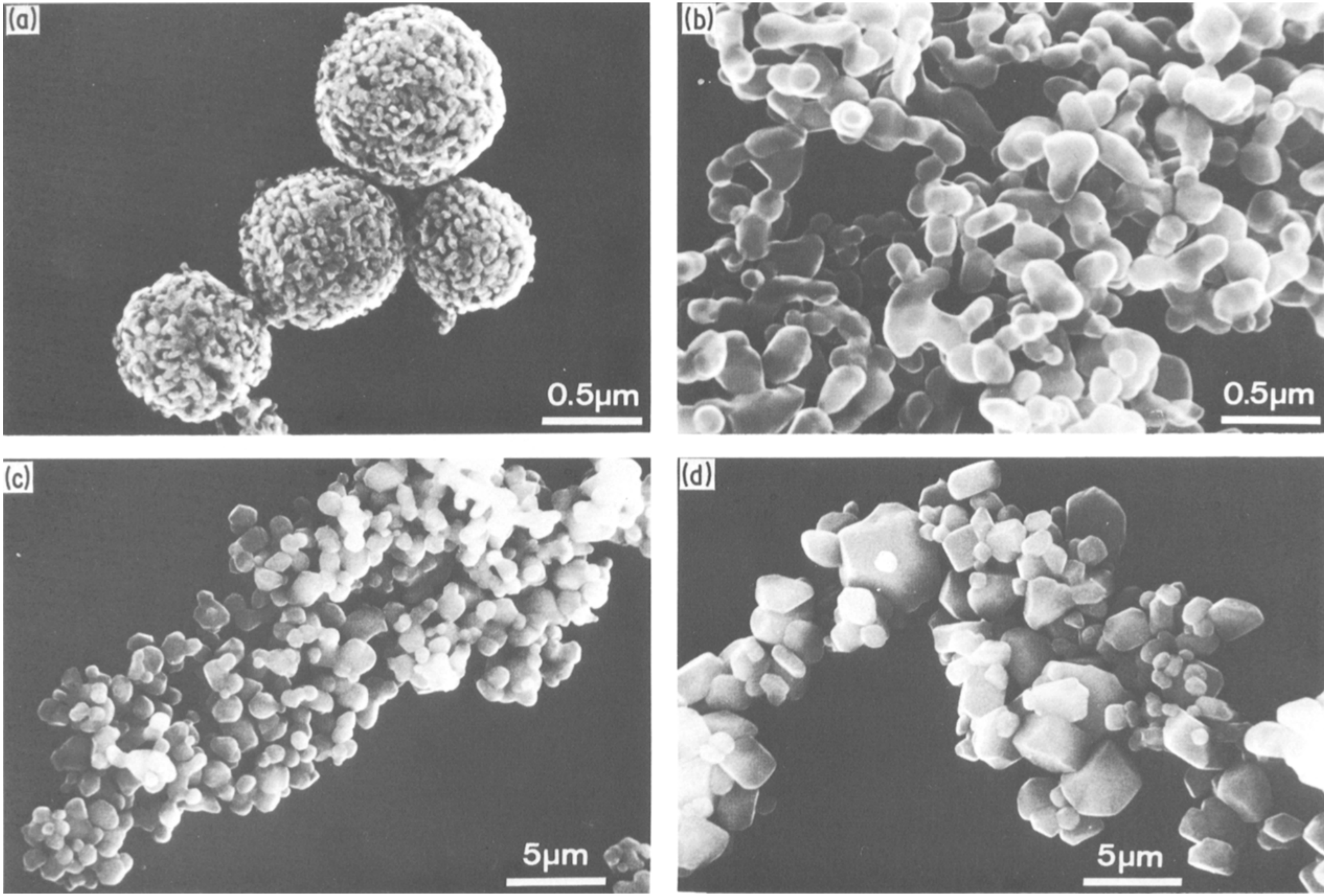

Figure 4 Scanning electron micrographs of hematite samples. (a) F600-4, (b) F700-16, (c) F900-16, (d) FV700-16.

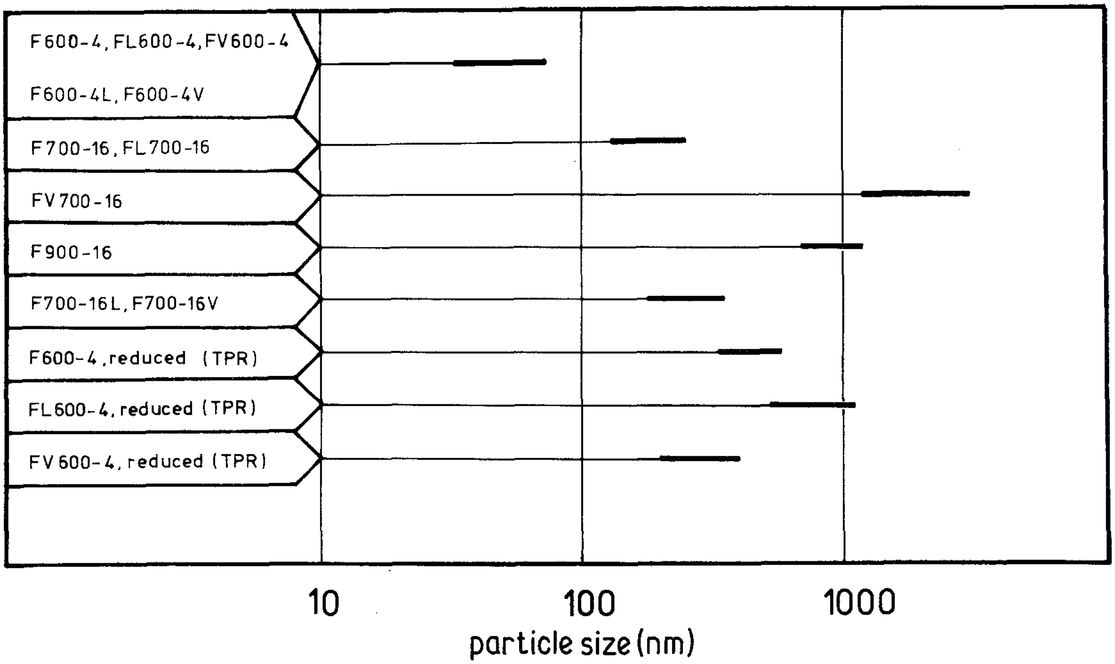

Figure 5 Particle size ranges for representative samples, as deduced from electron micrographs.

tives and their repartition in the bulk or on the surface of the solid reactant.

From Fig. 1 (Curves c to e) it is apparent that an increase of the time and/or the temperature of calcination tends to move the reduction peaks towards higher temperatures. By examining Fig. 5, this behaviour is clearly correlated with an increase of the particle size (compare samples F600-4, F700-16 and F900-16). The same correlation between particle size and reduction peak temperature is also found for the samples containing lithium (Fig. 2, curves a to c, and Fig. 5, samples FL600-4 and FL700-16) and vanadium (Fig. 3, curves a to e, and Fig. 5, samples FV600-4 and FV700-16). One may thus say that the particle size of hematite affects strongly its reducibility and has to be taken into account when discussing the effect of additives.

Fig. 5 shows that the presence of additives do not, in general, affect the particle size of hematite, whatever the calcination treatment used. Sample FV700-16 is, however, a striking exception. To explain it, the following observations might be of importance. After calcination treatment, sample FV700-16 was heavily agglomerated and was sticking to the porcelain boat; furthermore, the boat was contaminated with a yellow deposit, indicating probable segregation of vanadium pentoxide. The melting point of V_2O_5 is 685° C [25]; it is therefore reasonable to think that the segregation of liquid vanadium oxide is responsible for the considerable enhancement observed for the

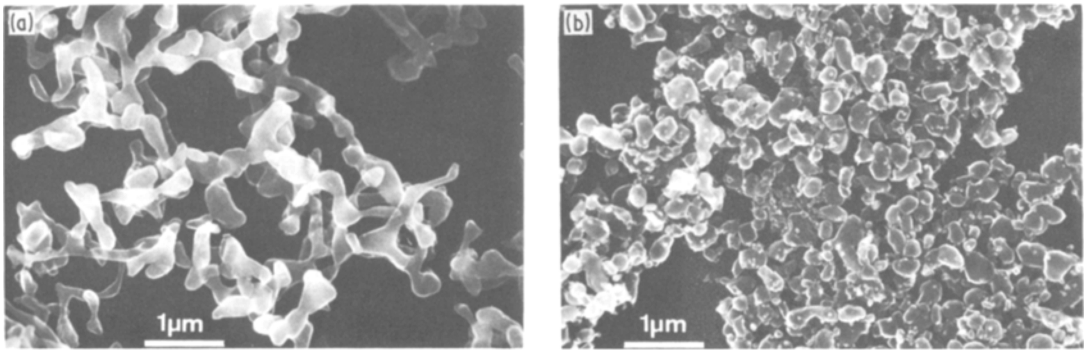

Figure 6 Scanning electron micrographs of samples after TPR run. (a) F600-4, (b) FV600-4.

sintering of hematite above 700° C. Indeed, examples of sintering promoted by a liquid phase are known [26].

The effect of additives on the reduction process itself may now be discussed, starting with the case of homogeneous samples. The effect of lithium is apparent when comparing the TPR patterns of the corresponding pure (Fig. 1, Curves a and d) and doped samples (Fig. 2, Curves a and c); in all cases the reduction peaks of the doped samples are observed at higher temperatures compared to the pure ones. The same comparison (compare Fig. 1a to Fig. 3a) shows that, when homogeneously distributed, vanadium has no marked effect on the reduction peaks of hematite. Nevertheless, Fig. 6 shows that the presence of this additive strongly affects the morphology of the iron particles obtained after complete reduction of hematite, by comparison with those obtained from the pure and lithium doped samples. This illustrates that all the possible effects of additives are not necessarily reflected by variations in the reducibility of hematite.

It is now interesting to compare the pure samples to the impregnated ones, in which the additives are spread on the surface of hematite. The TPR peaks for the samples impregnated with lithium (compare Fig. 2, Curves d and e, respectively to Curves a and d of Fig. 1) appear at higher temperatures than in the case of the corresponding pure samples, but still at a *lower* temperature than the corresponding homogeneous samples. This indicates that the retarding effect of lithium on the reduction process is most effective when it is present in the bulk of the solid. The case of vanadium is quite different: In contrast to homogeneous samples, the additive seems to bring about a retarding effect when introduced by impregnation. This effect increases markedly with the particle size of hematite. This is even more striking if we consider samples FV700-16 as being similar to impregnated samples, owing to the segregation of vanadium already discussed. Table II summarizes the mean particle sizes, calculated specific surface areas and surface concentrations of vanadium for the three samples considered here (F600-4V, F700-16V and FV700-16). Assuming all the vanadium is concentrated in a surface layer, a clear correlation appears between the calculated surface concentration of the additive and its inhibiting effect on the reduction process. A reasonable explanation is that vanadium oxide forms a hardly reducible coating on the surface of hematites, preventing its contact with the reducing gas. The figures in Table II support this interpretation: for sample F600-4V, the surface coverage is quite small while it is much more than one monolayer for sample FV700-16.

TABLE II Calculated surface concentration of vanadium

Sample	$\bar{D}$ (nm)	S* (m^2 g^{-1})	$(V)_s$† (atoms nm^{-2})
F600-4V	50	23	3.3
F700-16V	250	4.6	16
FV700-16	1900	0.6	120

*assuming particles are spheres

†assuming the complete segregation of vanadium on the surface of the particles.

5. Conclusions

A general conclusion coming from the present results is that a fair understanding of additive effects on the reactivity of solids, which have been the subject of many contradictory results in the past, can be gained by careful preparation and characterization of the tested solids.

In the case of the reducibility of hematite by hydrogen, a very important factor to be considered is the particle size of the solid. Any comparison of the effect of chemical additives should therefore necessitate the use of samples exhibiting comparable particle sizes.

The effect of an additive may be strongly affected by its actual repartition in the sample (bulk or surface). In the case of lithium, an inhibiting effect is always observed, but it appears to be the strongest when the additives is in true solid solution. On the contrary, vanadium exerts virtually no influence on the reducibility of hematite when present in solid solution. A strong inhibiting effect is observed in other cases, which can probably be ascribed to the accumulation of vanadium in the surface layers. After calcining the samples containing vanadium in solid soultion above the melting point of vanadium pentoxide, the inhibiting effect of the additive is enhanced by its strong promoting effect on the sintering of hematite.

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