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# Effect of mechanical activation on the synthesis of $\alpha$-$Fe_2O_3$–$Cr_2O_3$ solid solutions

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Continuous $\alpha$-$Fe_2O_3$–$Cr_2O_3$ solid solution series have been synthesized by two methods: (i) direct heating of coprecipitated hydroxides, and (ii) mechanical pre-treatment followed by heating. It is shown that mechanical treatment leads to a decrease in the preparation temperature of the solid solutions to 623 K. The formation of a continuous solid solution series by direct heating begins only at 773 K. The formation of the solid solutions was established by X-ray diffraction analysis, infrared and Mössbauer spectroscopy. The decrease in synthesis temperature of the $\alpha$-$Fe_2O_3$–$Cr_2O_3$ solid solutions is attributed to activation of the samples during their mechanical treatment. The samples obtained have large specific surface areas (up to 130 $m^2 g^{-1}$).

## 1. Introduction

It is known that $\alpha$-$Fe_2O_3$ and $Cr_2O_3$ form a continuous solid solution series on the basis of the close $Fe^{3+}$ (0.0645 nm) and $Cr^{3+}$ (0.0615 nm) ionic radii [1]. With rising $Cr_2O_3$ concentration, the lattice parameter decreases, due to the smaller ionic radius of the $Cr^{3+}$ [2]. During the formation of the continuous solid solution series, with increasing $Cr_2O_3$ content, the prevailing spin orientation changes from that characteristic of $\alpha$-$Fe_2O_3$ (at haematite concentration above 25%) to that corresponding to $Cr_2O_3$ [1, 3].

The solid solutions in the $Fe_2O_3$–$Cr_2O_3$ system have a catalytic effect on various reactions of industrial importance, such as oxidation of ammonia to nitrogen oxides, water–gas shift reaction [4–6]. The solid solutions are obtained above 800 K [7–12]. Data on the formation of the continuous solid solution series and the solubility regions at temperatures below 1000 K are somewhat contradictory. According to Atrostenko [5], samples of the $\alpha$-$Fe_2O_3$–$Cr_2O_3$ system calcined at 1023 K form a solid solution with a limited solubility. At $Cr_2O_3$ concentration above 30 wt % there is a second phase. On calcining a mixture of coprecipitated iron and chromium hydroxides at 773 K, Markin *et al.* detected the presence of a separate $Cr_2O_3$ phase in samples containing more than 20 wt % $Cr_2O_3$ [13]. Of course, the question arises whether it would be possible to synthesize a continuous solid solution series at temperatures below 800 K. The samples prepared at low temperatures should have large specific surface areas and a higher dispersity. These samples would be appropriate for catalysing the water–gas shift reaction.

It was therefore the purpose of the present work to obtain a continuous solid solution series at temperatures below 800 K using preliminary activation of the initial mixtures. A parallel comparison of the possibilities of preparation of this solid solution ($\alpha$-$Fe_2O_3$–$Cr_2O_3$) by the above method and by direct heating of the initial samples, is made.

## 2. Experimental procedure

The initial mixtures were prepared by addition of 2N $NH_4OH$ to $Fe(NO_3)_3 \cdot 9H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ solution at pH = 8. The preparation of $\alpha$-$Fe_2O_3$–$Cr_2O_3$ solid solutions was achieved in two ways: by direct heating and by mechanical pretreatment followed by heating of the initial samples. The calcination proceeded at 623, 723, 773 and 1173 K, and the duration of the isothermal heating was 8 h. The formation of solid solutions was studied on samples containing 10, 20, 35, 50 and 90 wt % $Cr_2O_3$. These samples were chosen on the basis of preliminary results. The mechanical treatment was performed with a Fritch planetary mill in a sintered corrundum bowl with grinding balls of the same material. The weight of the balls was 150 g, and that of the sample 10 g. The dry grinding method was used, which allowed contamination of the sample from the material of the bowl and the balls to be avoided. The grinding time was 2 h.

Three methods (X-ray diffraction (XRD) analysis, Mössbauer spectroscopy and infrared spectroscopy) were used to establish the formation of $\alpha$-$Fe_2O_3$–$Cr_2O_3$ solid solutions. The X-ray spectra were recorded using $CuK_\alpha$ radiation. The Mössbauer spectra were recorded at room temperature using a constant acceleration and computer registration. The radiation was obtained from a $^{57}Co$ source in a palladium matrix. The isomer shifts were obtained relative to an $\alpha$-Fe absorber. The infrared spectra were recorded in KBr. The maxima of the absorption bands were determined more precisely by self-deconvolution [14].

Thermal analysis of the samples was carried out at a heating rate of 10 °C $min^{-1}$.

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## 3. Results and discussion

Fig. 1 shows DTA curves of coprecipitated mixtures of iron and chromium hydroxides. The curves reveal an endothermic effect of dehydration to oxides and an exothermic effect of crystallization at a maximum at 713–773 K. With rising percentage of $Cr_2O_3$, the crystallization process is shifted to higher temperatures (Fig. 1a–d).

The specific surface areas of the samples decrease with increasing calcination temperature as sintering and crystallization proceed (Table I). The low-temperature sintering in the $Fe_2O_3$–$Cr_2O_3$ system proceeds even at temperatures of 623–723 K. A similar process has also been observed with pure oxides $Fe_2O_3$ and $Cr_2O_3$ [15–17]. The Table indicates that the specific surface areas of the samples containing 35 and 20 wt % $Cr_2O_3$ and obtained at 623–723 K, are higher.

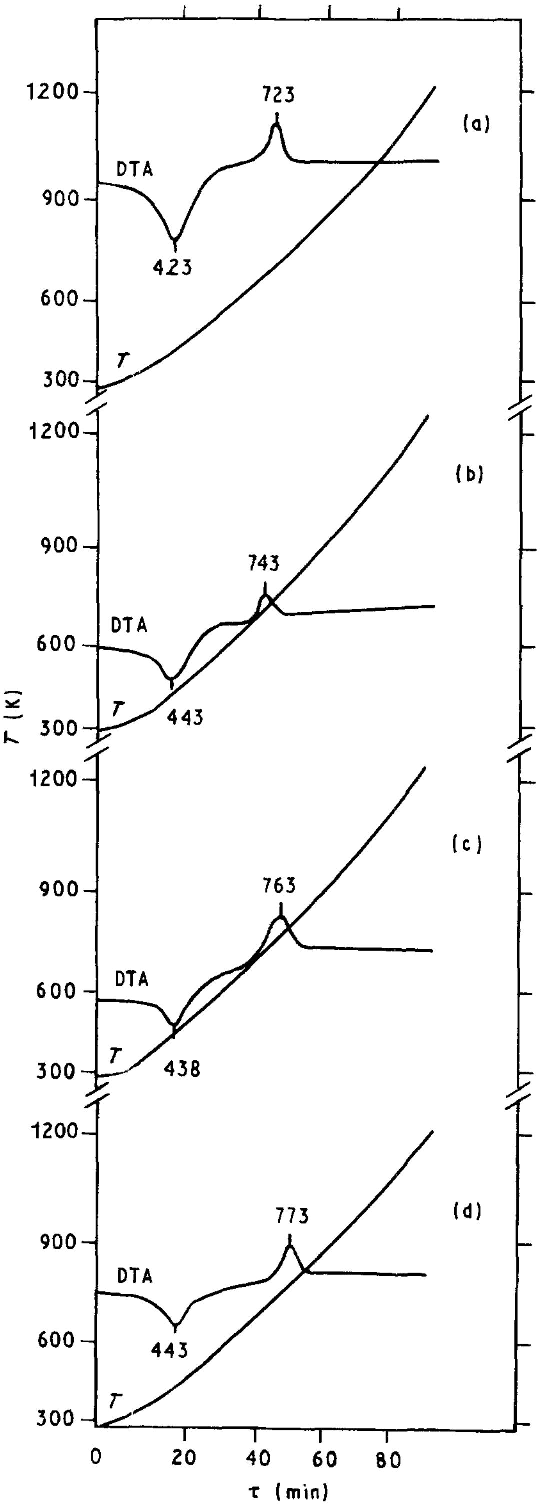

*Figure 1* DTA of coprecipitated samples: (a) $Fe(OH)_3 + Cr(OH)_3$ (10 wt % $Cr_2O_3$), (b) $Fe(OH)_3 + Cr(OH)_3$ (20 wt % $Cr_2O_3$), (c) $Fe(OH)_3 + Cr(OH)_3$ (50 wt % $Cr_2O_3$), (d) $Fe(OH)_3 + Cr(OH)_3$ (90 wt % $Cr_2O_3$).

The main method used by us for registration of the solid solution formation in the $Fe_2O_3$–$Cr_2O_3$ system was XRD analysis. Fig. 2 illustrates a typical dependence of the interplanar distance, *d*, on the percentage of $Cr_2O_3$ for a sample synthesized by mechanical treatment and heating at 773 K. The error in the determination of the interplanar distance is also shown. It can be seen that with rising $Cr_2O_3$, *d* decreases gradually indicating the formation of a continuous solid solution series [12]. The interplanar distance for all samples forming solid solution series are within error limits. The XRD analysis data indicate that continuous solid solution series are obtained with: (a) samples mechanically treated and heated at 623, 723, 773 and 1173 K, (b) samples directly heated at 773 and 1173 K.

The samples prepared by direct calcination at 623 K form no continuous solid solution series. Thus, the X-ray patterns of the sample containing 10 wt % $Cr_2O_3$ exhibit strongly broadened peaks, which is an indication of the insufficient crystallization of the solid solution formed. The samples containing 20 and 35 wt % $Cr_2O_3$ are amorphous. With further increase in $Cr_2O_3$ content, the samples become crystalline again, but a $Cr_2O_3$ phase is also observed. The interplanar distance of these samples is beyond error limits. The samples obtained by direct heating at 723 K form a $Fe_2O_3$–$Cr_2O_3$ solid solution with a limited solubility.

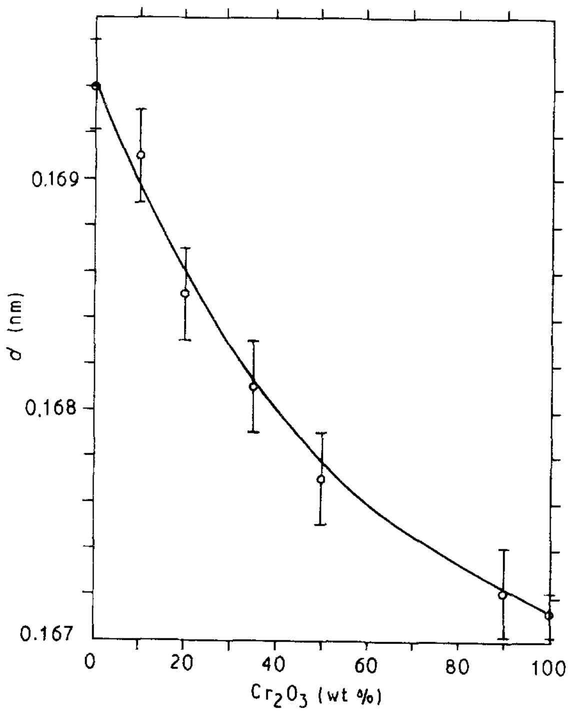

*Figure 2* Change in the interplanar distance, *d*, with increasing $Cr_2O_3$ content, showing a typical dependence for a sample prepared by mechanical treatment and heating at 773 K.

TABLE I Specific surface areas of the samples

| $Cr_2O_3$ (wt %) | Preparation method | Specific surface areas ($m^2 g^{-1}$) | | | |
|---|---|---|---|---|---|
| | | 623 K | 723 K | 773 K | 1173 K |
| 10 | Mechanical treatment | 98 | 66 | 46 | 9 |
| | Direct heating | 111 | 57 | 51 | 10 |
| 20 | Mechanical treatment | 126 | 62 | 51 | 16 |
| | Direct heating | 118 | 60 | 54 | 13 |
| 35 | Mechanical treatment | 132 | 76 | 63 | 14 |
| | Direct heating | 110 | 64 | 59 | 11 |
| 50 | Mechanical treatment | 108 | 49 | 42 | 9 |
| | Direct heating | 96 | 41 | 33 | 7 |
| 90 | Mechanical treatment | 56 | 36 | 28 | 8 |
| | Direct heating | 31 | 20 | 18 | 8 |

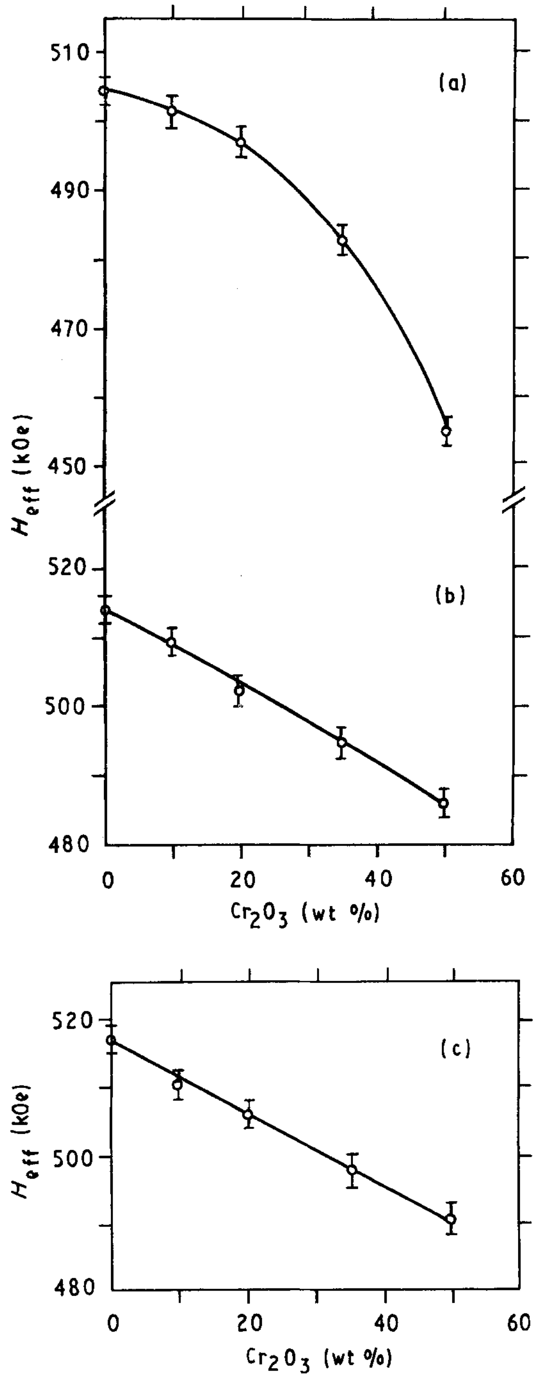

*Figure 3* Change in internal magnetic field, $H_{eff}$, of samples prepared by mechanical treatment and heating at (a) 623 K, (b) 723 K and (c) 773 K.

With increasing $Cr_2O_3$ concentration above 10 wt %, a separate $Cr_2O_3$ phase appears.

It is typical of all samples that with rising calcination temperature the peaks in the X-ray pattern become narrower and more intense.

Fig. 3 shows the values of the internal magnetic field, $H_{eff}$, calculated from the Mössbauer spectra of samples synthesized by mechanical treatment and heated at 623–773 K. It was found that $H_{eff}$ is the Mössbauer parameter that displays the most pronounced change after the formation of $Fe_2O_3$–$Cr_2O_3$ solid solutions. With increasing $Cr_2O_3$ content, the internal magnetic field value decreases (Fig. 3a–c). The Mössbauer spectrum of the sample containing 90 wt % $Cr_2O_3$ is a doublet (paramagnetic effect) and determination of $H_{eff}$ in this case is impossible. The decrease in internal magnetic field value has also been established by other authors [1, 7, 8, 10]; however, for $\alpha$-$Fe_2O_3$–$Cr_2O_3$ solid solutions synthesized at temperatures significantly higher than 773 K, the decrease in $H_{eff}$ is attributed to "magnetic dilution" of the $\alpha$-$Fe_2O_3$–$Cr_2O_3$ system with increasing $Cr_2O_3$ content. In addition, the decrease in the synthesis temperature leads to a decrease in value of the internal magnetic field of the samples. The lowest value corresponds to the sample obtained at 623 K. The alteration of $H_{eff}$ with temperature can be ascribed to the defect structure of the solid solutions synthesized at low temperatures. The XRD data also confirm this explanation. A decrease in the internal magnetic field with decreasing of calcination temperature was also found for disperse $\alpha$-$Fe_2O_3$ [15].

The Mössbauer spectroscopy method is suitable for studying the $\alpha$-$Fe_2O_3$–$Cr_2O_3$ solid solutions. However, its application is restricted at high $Cr_2O_3$ concentrations due to the presence of a paramagnetic effect.

Infrared spectroscopy is also used for registering the $\alpha$-$Fe_2O_3$–$Cr_2O_3$ solid solutions obtained at low temperatures. Fig. 4 presents the infrared spectra of the samples synthesized by mechanical treatment and heating at 623 K. Fig. 5 shows the correlation between the shift of the absorption band maxima and the percentage of $Cr_2O_3$. The data are taken after self-deconvolution of the spectra shown in Fig. 4. Obviously this shift is linear, which is indicative of the

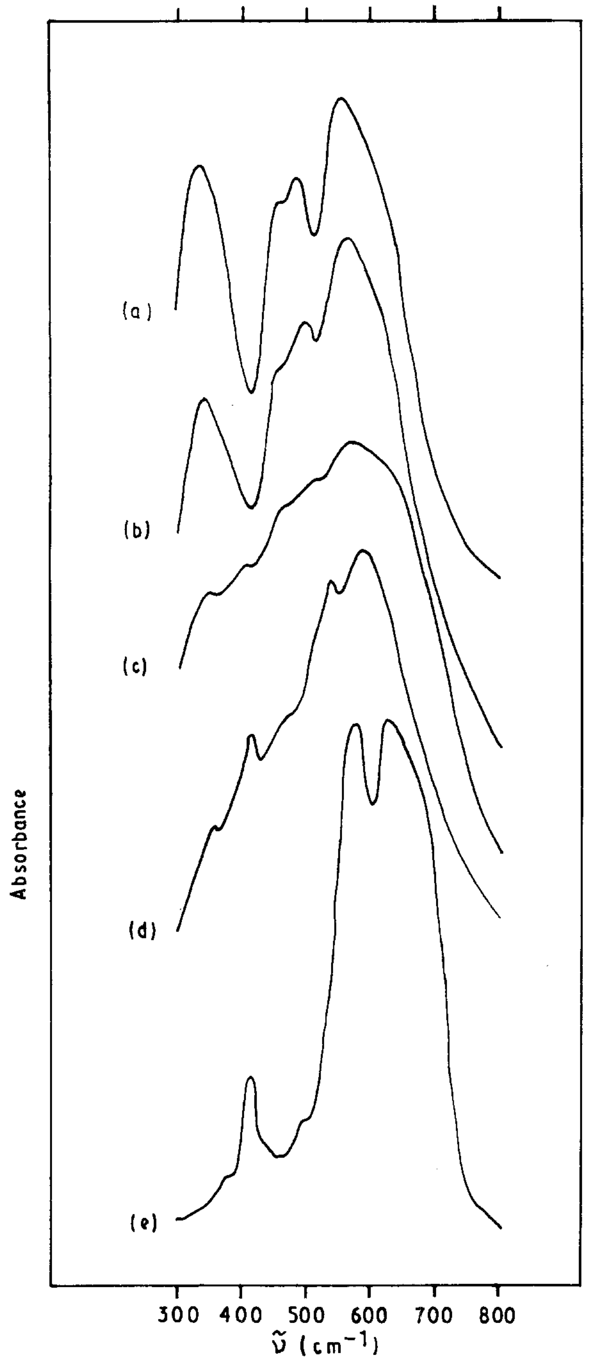

*Figure 4* Infrared spectra of samples prepared by mechanical treatment and heating at 623 K: (a) 10 wt% $Cr_2O_3$, (b) 20 wt% $Cr_2O_3$, (c) 35 wt% $Cr_2O_3$, (d) 50 wt% $Cr_2O_3$, (e) 90 wt% $Cr_2O_3$.

formation of a continuous $\alpha$-$Fe_2O_3$–$Cr_2O_3$ solid solution series [11].

The results from Mössbauer and infrared spectroscopies also confirm the XRD data.

## 4. Conclusion

Mechanical treatment of coprecipitated hydroxides allows the synthesis of continuous solid solution series at 623 K. Direct heating of the initial mixtures leads to the formation of continuous solid solution series only at 723 K. The decrease in the formation temperature of the solid solutions can be explained by the effect of sample activation by their mechanical treatment, which accelerates the solid phase diffusion processes.

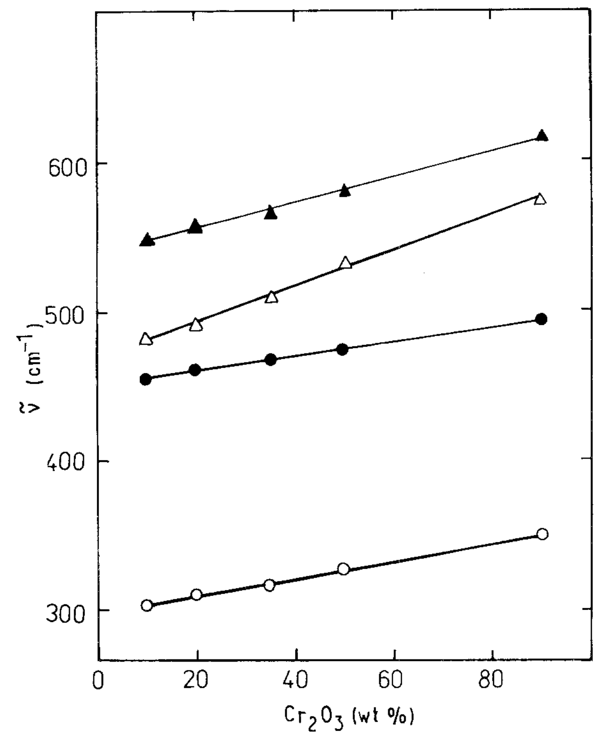

*Figure 5* Shift of the absorption band maxima with increasing percentage of $Cr_2O_3$ for samples obtained by mechanical treatment and heating at 623 K. Maxima of bands at (○) 313 cm$^{-1}$, (●) 452 cm$^{-1}$, (△) 485 cm$^{-1}$ and (▲) 552 cm$^{-1}$ for 10 wt% $Cr_2O_3$. The original infrared spectra are shown in Fig. 4.

The solid solutions obtained at 623–723 K are expected to exercise a good catalytic effect towards the water–gas shift reaction, which proceeds at a temperature close to those given above. The samples prepared within this temperature range have large specific surface areas.

The formation temperature of continuous solid solution series $\alpha$-$Fe_2O_3$–$Cr_2O_3$ depends on the preparation conditions. Mechanical activation can lead to a decrease in the synthesis temperature of the solid solutions of other oxide systems.

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