

Electrical conductivity and chemical reactivity of hydrous ferric oxides

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Abstract. Hydrous ferric oxide was synthesised under alkaline conditions, aged in distilled water and calcined. Characterisation was attempted through x-ray, differential thermal analysis, thermogravimetric and infrared analyses. Electrical conductivity was measured and chemical reactivity towards hydrazine investigated. It was found that ageing as well as calcination facilitated crystallisation to α -Fe₂O₃ and thereby decrease the reactivity, which in turn appears to be strongly influenced by the three types of water, viz. absorbed, bound and crystallisation.

Keywords. Electrical conductivity; chemical reactivity; hydrous ferric oxides.

1. Introduction

Hydrous ferric oxides have been extensively studied (Weiser and Milligan 1935; Gheith 1952; Ramachandran and Bhattacharyya 1954; Blyholder and Richardson 1962; Okamoto *et al* 1967; Menezes 1977; Nagvekar 1977). X-ray diffraction, differential thermal analysis (DTA), thermogravimetric (TG), infrared (IR), and electrical conductivity techniques have been employed to determine the effect of ageing in distilled water on the structure and properties. However, an overall correlation cannot be attempted since the various data refer to different samples prepared from starting materials of different purity and under different preparative conditions. Besides, the electrical conductivity has not been reported beyond 50° C. Therefore, it was considered worthwhile to synthesise hydrous ferric oxides and to study the effect of ageing and calcination on the structure and chemical reactivity towards hydrazine. Electrical conductivity was also measured from 25° to 400° C.

2. Experimental

Ferric oxide gel was prepared by the method of Okomoto *et al* (1967). The precipitate of ferric oxide obtained by mixing 0.1 M Fe(NO₃)₃ and 6 M NH₄OH was washed with water and aged in distilled water at 26° C for 0, 15, 30 and 56 days

respectively. It was then dried at room temperature for 60 hr in a vacuum desiccator and heated in an oven to dryness at 100° C for 10 hr. The samples were ground to -200 to +300 mesh size and calcined in air at 110°, 200°, 300° and 400° C for 10 min each respectively.

X-ray diffraction patterns were recorded at room temperature using CoK_α radiation ($\lambda = 1.790 \text{ \AA}$). Thermogravimetry was carried out in air upto 450° C with a constant heating rate of 6° C/min. The DTA curves were recorded in air upto 500° C using Al_2O_3 as the standard and a heating rate of 6° C/min. IR spectra were recorded at room temperature using KBr pellet with NaCl prism in the range 600–4000 cm^{-1} . DC electrical conductivity of polycrystalline pellets (~2 cm in diameter and ~0.3 to 0.5 cm thickness) was measured in air, at temperatures from 25° to 400° C.

The chemical reactivity of the various compositions was studied through decomposition of hydrazine sulphate as a function of ageing for different periods of time and calcination at 110°, 200°, 300° and 400° C respectively.

3. Results and discussion

3.1 X-ray diffraction analysis

In view of the existence of several ferric oxides with varying chemical compositions and structures, characterisation with only x-ray diffraction analysis becomes difficult. For example, the following oxides are known to exist: $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$, $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, $\gamma\text{-FeO(OH)}$, $\delta\text{-FeOOH}$ and $\beta\text{-FeOOH}$. However the observed x-ray diffraction peaks corresponded only to $\alpha\text{-FeOOH}$ or $\alpha\text{-Fe}_2\text{O}_3$, since only the following d_{hkl} values were obtained: 2.69, 2.44, or 2.69, 2.51, 1.69 \AA . The lines corresponding to 2.56, 2.26 and 1.64 \AA respectively were not observed, suggesting the absence of $\gamma\text{-FeO(OH)}$, $\delta\text{-FeOOH}$ and $\beta\text{-FeOOH}$. The results of the x-ray data have been summarised in table 1. It will be seen that non-aged and 15-day aged samples start crystallising after heating above 200° C, while 30-day and 56-day aged samples crystallised at > 110° and 110° C respectively. Anhydrous $\alpha\text{-Fe}_2\text{O}_3$ was formed, in general, on calcining at higher temperatures. These results which agree with previous reports (Weiser and Milligan 1935; Okamoto *et al* 1967; Furuichi *et al* 1969) indicate that ageing facilitates crystallisation. All other specimens exhibited only diffuse peaks indicating the absence of crystallinity.

3.2 Differential thermal analysis and thermogravimetry

Depending on the ageing period and the temperature of calcination, DTA curves exhibited endothermic peaks occurring around 110°, 170° and 275° C respectively. The peak at 110° C is due to removal of physically adsorbed water; the other two are due to expulsion of two differently bonded types of water. This is indicated by the grossly different values of activation energy, viz. 0.3 kcal/mol for the water removed at 170° C and 21 kcal/mol for the water expelled at 275° C respectively. Water corresponding to the endothermic peak at 170° C on the DTA curve, or expelled between 110° and 220° C as seen in the TG curves will henceforth be designated as bound water (Okamoto *et al* 1967). Following

Table 1. X-ray analysis of hydrous ferric oxides.

Ageing period	Calcination temperature °C	Observation
Non-aged	110	Amorphous
	200	Amorphous
	300	$\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
	400	$\alpha\text{-Fe}_2\text{O}_3$
15 days	110	Amorphous
	200	Amorphous
	300	$\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
	400	$\alpha\text{-Fe}_2\text{O}_3$
30 days	110	Amorphous
	200	$\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
	300	$\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
	400	$\alpha\text{-Fe}_2\text{O}_3$
56 days	110	$\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
	200	$\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
	300	$\alpha\text{-Fe}_2\text{O}_3$
	400	$\alpha\text{-Fe}_2\text{O}_3$

Bhattacharyya (1957), water corresponding to the DTA peak at 275° C will be referred to as crystallisation water.

The samples were heated to 110° C for a sufficient length of time to remove the adsorbed water. The observed mass-losses in conjunction with DTA and IR data were used to determine the weight percentage of bound and crystallisation water. The data presented in table 2 show that, with increasing ageing period, the percentage of bound water progressively decreases, while an almost constant amount of crystallisation water appears only after ageing for about 15 days.

3.3 Infrared analysis

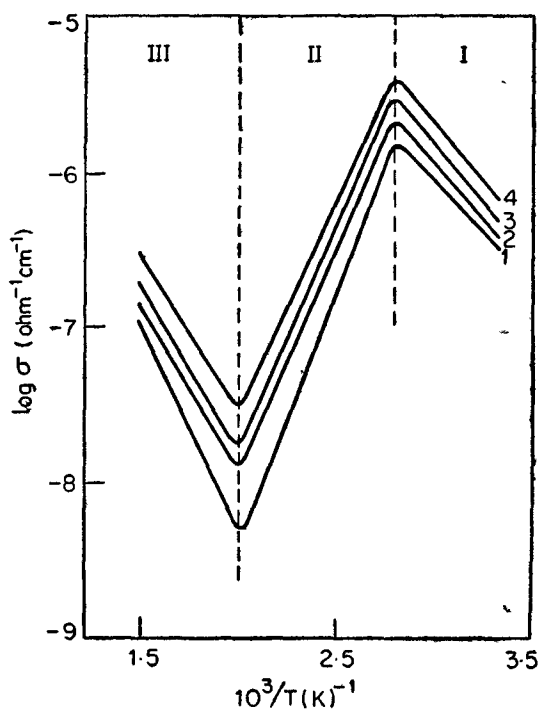
Nobuoka (1965) and Glemser and Hartert (1956) reported the IR spectra of hydrous ferric oxides and ascribed the bands at 3250 cm^{-1} and 1620 cm^{-1} to bound water -OH stretching and bending respectively. Two additional bands at 900 cm^{-1} and 810 cm^{-1} were attributed to the presence of crystallisation water. In the present study, these criteria were used, in conjunction with DTA and TG results, to determine the respective percentages of bound and crystallisation water (table 2).

3.4 Electrical conductivity

Our results for non-aged and aged specimens are depicted in figure 1. Three regions I, II and III can be clearly seen. Region I extends from room temperature

Table 2. Bound and crystallisation water in hydrous ferric oxides.

Ageing period	Calcination temperature °C	Amount of water	
		Bound %	Crystallisation %
Non-aged	110	8.4	Nil
	200	6.9	Nil
	300	5.2	Nil
	400	2.5	Nil
15 days	110	5.8	2.3
	200	4.8	2.1
	300	0.8	0.6
	400	0.6	0.4
30 days	110	3.2	2.7
	200	3.0	1.7
	300	0.8	0.6
	400	Nil	Nil
56 days	110	2.9	3.0
	200	2.8	1.9
	300	0.8	0.7
	400	Nil	Nil

**Figure 1.** Electrical conductivity of hydrous ferric oxides. 1. Non-aged, 2. Aged for 15 days; 3. Aged for 30 days; 4. Aged for 56 days.

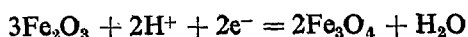
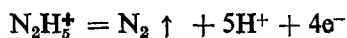
to about 50° C and corresponds to the removal of adsorbed water. Region II corresponds to the temperature range 90–235° C in which the bound water is continuously being driven away, as evidenced by DTA, TG and IR measurements. In region III, the crystallisation water slowly goes away. Comparison of non-aged, 15, 30 and 56 day-aged specimens indicates that, with increasing ageing period, the curve progressively shifts upwards. This is also equivalent to a decrease in percentage of bound water (table 2). On calcining at increasingly higher temperatures, viz. 110°, 200°, 300° and 400° C respectively, an analogous conductivity behaviour was observed. Further, crystallisation water appears to affect the conductivity only negligibly since the behaviour for all the samples is similar in region III despite the fact that the non-aged sample did not contain any crystallisation water (table 2).

Table 3. Amount of hydrazine decomposed by hydrous ferric oxides aged for various periods and calcined at different temperatures.

Ageing period	Calcination temperature ° C	Reaction time hr	Amount of hydrazine decomposed ($\times 10^{+2}$ g)	Ageing period	Calcination temperature ° C	Reaction time hr	Amount of hydrazine decomposed ($\times 10^{+2}$ g)	
Non-aged	110	24	0.56	15 days	110	24	0.14	
		46	0.61			46	0.19	
		72	0.66			72	0.23	
	200	24	0.82		200	24	0.17	
		46	0.91			46	0.17	
		72	0.95			72	0.24	
	Non-aged	300	24	0.35	30 days	300	24	0.13
			46	0.47			46	0.18
			72	0.47			72	0.18
400		24	0.14		400	24	0.08	
		46	0.22			46	0.10	
		72	0.25			72	0.13	
Non-aged	110	24	0.29		110	24	0.01	
		46	0.38			46	0.01	
		72	0.40			72	0.01	
	200	24	0.33		200	24	0.06	
		46	0.35			46	0.06	
		72	0.35			72	0.06	
15 days	300	24	0.13	56 days	300	24	0.08	
		46	0.14			46	0.09	
		72	0.16			72	0.10	
	400	24	0.06		400	24	0.06	
		46	0.09			46	0.06	
		72	0.12			72	0.06	

3.5 Decomposition of hydrazine over hydrous ferric oxides

An oxide sample (0.5 g) was immersed in a mixture of aqueous solutions of 0.4 N $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ (5 ml) and 0.5 N NaOH (15 ml) and the amount of decomposition of hydrazine after immersion for 24 hr was determined iodometrically. The decomposition reaction may be represented by



The results presented in table 3 show that the chemical reactivity increases from 110° to 200° C and then steadily decreases. This indicates that the presence of bound water unaccountably decreases the reactivity so that at 200° C, the reactivity is highest when most of the bound water has been expelled. On further increasing the calcination temperature, the tendency to crystallise to $\alpha\text{-Fe}_2\text{O}_3$ increases and, therefore, the reactivity decreases.

4. Conclusion

The chemical reactivity and probably, the catalytic activity of hydrous ferric oxides is strongly influenced by the three types of water present in it. The amounts of the different types of water are, in turn, influenced by ageing, calcination and preparative conditions.

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