A STUDY ON THE THERMAL DECOMPOSITION OF IRON-COBALT MIXED HYDROXIDES

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Thermal decomposition of pure $Fe(OH)_3$ and mixed with $Co(OH)_2$ were studied using TG, DTA, kinetics of isothermal decomposition and electrical conductivity measurements. The thermal products were characterized by X-ray diffraction and IR spectroscopy. The TG and DTA analysis revealed the presence of Co^{2+} retards the decomposition of ferric hydroxide and the formation of $\alpha\text{-}Fe_2O_3$. The kinetics of decomposition showed that the mixed samples need higher energy to achieve thermolysis. The investigation of thermal products of mixed samples indicated the formation of cobalt ferrite on addition of $x = 1$ or 1.5 cobalt hydroxide. The electrical conductivity accompanying the thermal decomposition decreases in presence of low ratio of Co^{2+} ($x = 0.2$) via the consumption of holes created during thermal analysis. The continuous increase in σ values on increasing of Co^{2+} concentration corresponded to the electron hopping between Fe^{2+} and Co^{3+}.

Keywords: DTA, electrical conductivity, mixed hydroxides, TG

Introduction

In an increasing number of areas of technology and, hence industry progress is recognized as being directly related to understanding the factors influencing the reactivity of solids how their reaction and interaction in specific environments. It was found [2, 3] the active sites as well as the electronic structure of the semiconducting surface are changed in presence of foreign cations. However, in view of the oxide-oxide interaction at appropriate temperature, knowledge of the thermal behaviour becomes an essential prequist to understand the texture, semiconducting and catalytic properties of the thermal products. Therefore, the present investigation was devoted to study the thermal decomposition of iron-cobalt hydroxides system. On the other hand, the solid substances produced from the thermal decomposition are characterized by using different techniques. The

techniques employed in this work are TG, DTA, kinetics of isothermal decomposition, electrical conductivity accompanying the thermal processes, X-ray diffraction and IR spectroscopy.

Experimental

Materials

Analar grade chemicals were used throughout. Mixed samples of iron and cobalt hydroxides (the mole content of Co^{2+} is $x = 0.2$, 1 or 1.5) were prepared by co-precipitation of the metal hydroxides followed by drying in an oven at 100°C. Cobalt nitrate, ferric chloride, ferrous ammonium sulphate and sodium hydroxide were used in this study. The details of the reaction equations were reported elsewhere [4, 5].

Techniques

Thermogravimetric (TG) and differential thermal analysis (DTA) of pure iron and cobalt hydroxides and their mixtures were carried out in air atmosphere using an automatically recording thermobalance, type 160 KS (West Germany). The heating rate was kept at 10 deg·min^{-1} and 20 mg sample of each solid specimen was employed in each experiment. α-alumina powder for DTA standard material was applied as a reference. Kinetics of isothermal decomposition of samples was studied in atmospheric pressure using Sartorious thermobalance (type 7085-02).

The d. c electrical conductivity was measured using the method described previously [6]. The data were obtained in presence of air atmosphere and the heating rate was adjusted to 10 deg·min^{-1}.

X-ray diffraction (XRD) of the thermal products of pure and mixed samples were performed with Philips diffractometer (type PW 2103) using a Cu target and Ni filter. The diffraction lines of the characterized samples were matched with the ASTM cards [7].

IR absorption spectra of calcined samples were obtained by KBr technique in the range of 1600–200 cm^{-1}, using Perkin Elmer model 599B infrared spectrophotometer.

Results and discussion

Thermal analysis

TG and DTA curves of pure $Fe(OH)_3$, $Co(OH)_2$ and their mixtures are represented in Fig. 1. Curve (a) illustrates the TG and DTA analysis of pure $Fe(OH)_3$.

It shows that the decomposition process takes place in three stages. The first endothermic peak located at 100°C corresponds to the loss of adsorbed water. The second broad endothermic peak maximized at 240°C corresponds to the thermal decomposition of Fe(OH)$_3$ to amorphous γ-Fe$_2$O$_3$ [8]. It was observed that all compounds undergo crystal structure changes with rising temperature [9, 10], in all cases it is the transformation of a lattice of cubic symmetry into an α-rhombohedral lattice which is stable at high temperature. The stability of α-compounds is strongly influenced by the preparation method, particle size [11], oxidation extent of initial phase [12], composition and nature of cation present [13]. Thus the third exothermic peak located at 500°C which accompanied without weight loss on the TG curve attributed to the phase transition i.e. γ-Fe$_2$O$_3$ $\rightarrow \alpha$-Fe$_2$O$_3$ [14]. The X-ray diffraction patterns of Fe(OH)$_3$ calcined at different temperature are shown in Fig. 2 (curve a).

It appears that the sample calcined at 250°C corresponds to the second decomposition stage on the DTA curve Fig. 1, indicates the formation of γ-Fe$_2$O$_3$. The presence of this phase is stable on heating the original sample up to 350°C. On the other hand, the sample calcined above 350°C gave new lines which confirm the formation of α-Fe$_2$O$_3$. The IR spectra of the same samples characterized by X-ray shown in Fig. 3 (curve a). It should be noted that the bands assigned at 680, 630, 550 and 440 cm^{-1} of the sample calcined at 250, 300 and 350°C corresponds to γ-Fe$_2$O$_3$ while the shift in the position of these bands to lower wave number is probably due to the variation of the lattice structure from γ to α-Fe$_2$O$_3$ [15].

Curve (e) of pure Co(OH)$_2$ indicates that the DTA exhibits three decomposition steps. The first endothermic peak maximized at 120°C can be related to the removal of water of hydration while the second endothermic peak maximized at 240°C attributed to the decomposition of Co$_2$O$_3\cdot$H$_2$O to Co$_3$O$_4$ [16]. The sharp and strong endothermic peak with its maximum at 920°C which accompanied with a weight loss on TG curve denotes that Co$_3$O$_4$ decomposes to CoO [17–19]. X-ray diffraction patterns of Co(OH)$_2$ calcined at different temperatures are presented in Fig. 2 (curve b). It shows that Co$_3$O$_4$ developed on heating the original sample at 250°C, the further heating up to 600°C leads to an increase in the intensity of the characteristic lines of Co$_3$O$_4$. Moreover, the IR spectra of the same samples investigated by X-ray diffraction are shown in Fig. 3 (curve b). Comparing these bands with these predomined by Nyquist and Kagel [20], the two bands assigned at 660 and 560 cm^{-1} characterizing a Co$_3$O$_4$ structure [21].

The influences of cobalt hydroxide addition on the thermal decomposition processes of ferric hydroxide are shown in Fig. 1, curves b, c and d for $x = 0.2$, 1 and 1.5 respectively. These curves reveal that the addition of 0.2 increases the maximum decomposition temperature and the phase transformation ($\gamma \rightarrow \alpha$-Fe$_2O_3$) to higher values. This indicates that the addition of low ratio from cobalt ions generally retards the formation of α-Fe$_2$O$_3$ solid. This result is in good agreement with the result obtained by Barriga *et al.* [8].
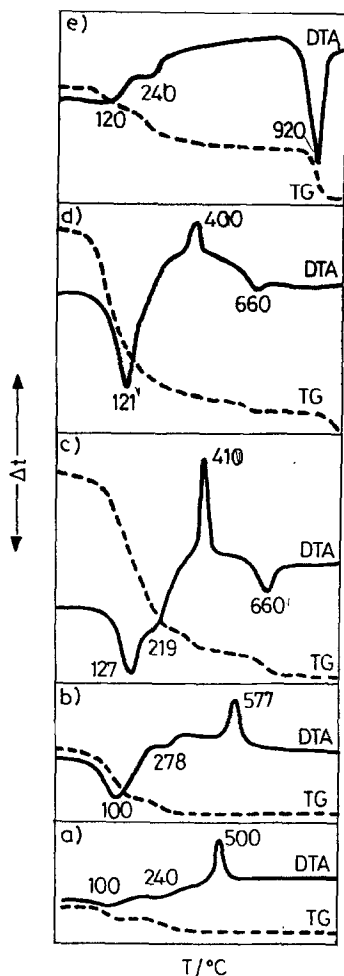
Fig. 1 DTA and TG curves of pure $Fe(OH)_3$ and mixed with 0.2 Co^{2+}(b), $1Co^{2+}$(c) and $1.5Co^{2+}$ ions (d), [curve e of pure $Co(OH)_2$]

The DTA curves of $Fe(OH)_3$ mixed with $x = 1$ or 1.5 (curves c and d) added two new peaks maximized at 410° and 660°C. The first exothermic peak is probably caused by the formation of cobalt ferrite spinel [8]. The second one accompanied with a weight loss can be explained on the basis of the cation distribution and literary antecedents [22, 23]. This effect can be associated with O_2 release, where, by a cation-deficient, cobalt ferrite becomes a mixture of stoichiometric $CoFe_2O_4$ and the iron sesquioxide phase stable at this temperature, α-Fe_2O_3. The X-ray patterns of the mixed hydroxides calcined at 600°C are represented in Fig. 4 (curve a). Comparing these patterns with those identified in the ASTM cards [7], the results show that at lower Co_3O_4 mixing ratio ($x = 0.2$), the
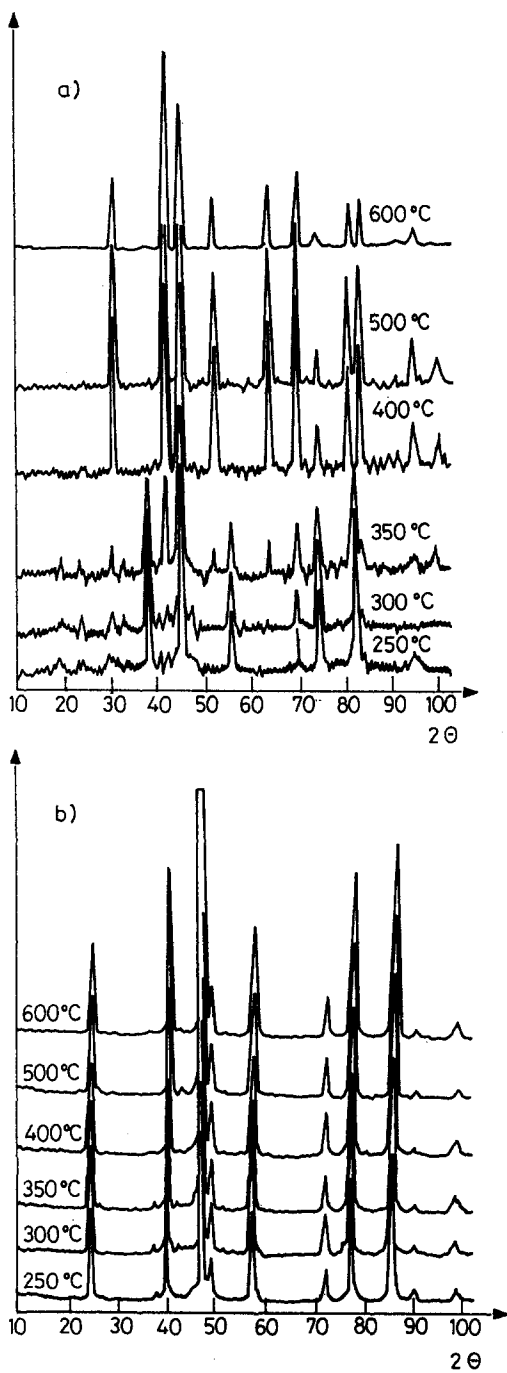
Fig. 2 X-ray diffraction patterns of the calcination products of $Fe(OH)_3$ (a) and $Co(OH)_2$ (b)

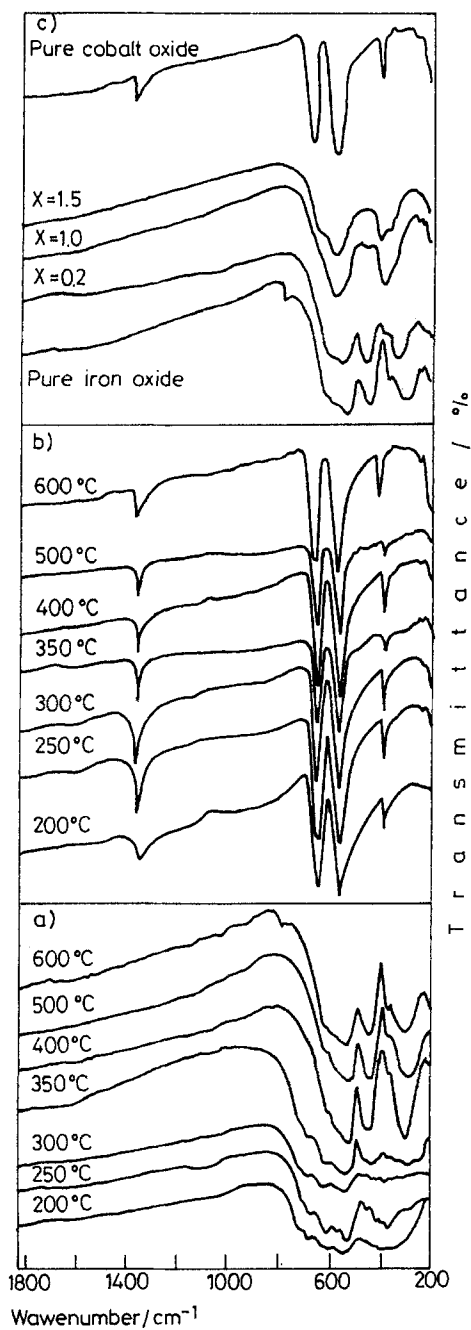**Fig. 3** IR spectra of the calcination products of pure Fe(OH)₃ (*a*), pure Co(OH)₂ (*b*) and their
mixture (*c*)

predominant diffraction lines are corresponding to a α-Fe_2O_3, the most intense lines located at $d(Å)$ = 3.54, 2.63, 2.46, 2.16, 1.81 and 1.44 corresponding to I/I_o = 100.0, 67.6, 24.4, 24.8, 36.0 and 23.6. On increasing Co_3O_4 mixing ratios (x = 1 or 1.5), the spinal lattice structure $CoFe_2O_4$ is formed reaching maximum at the
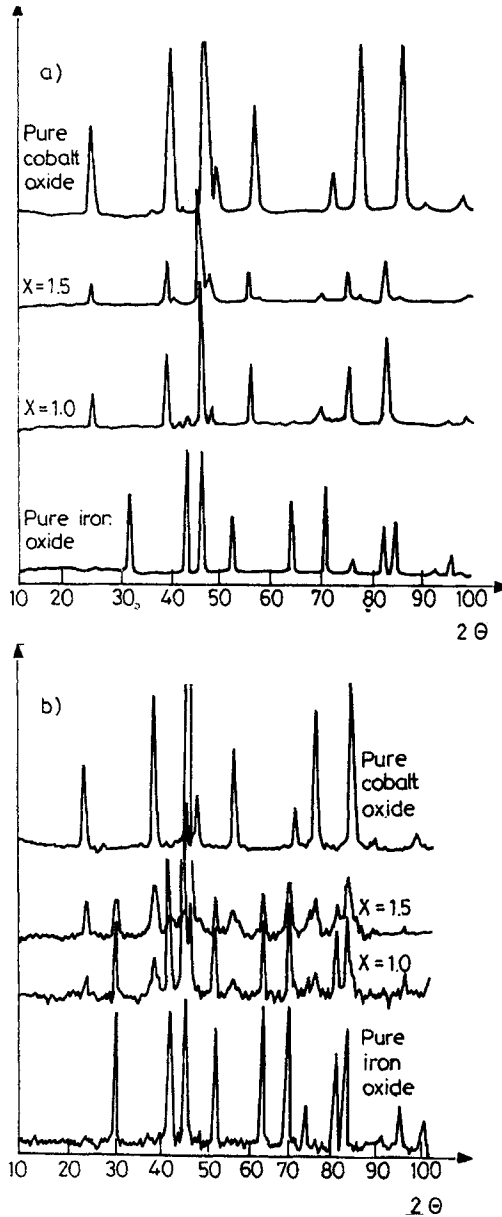

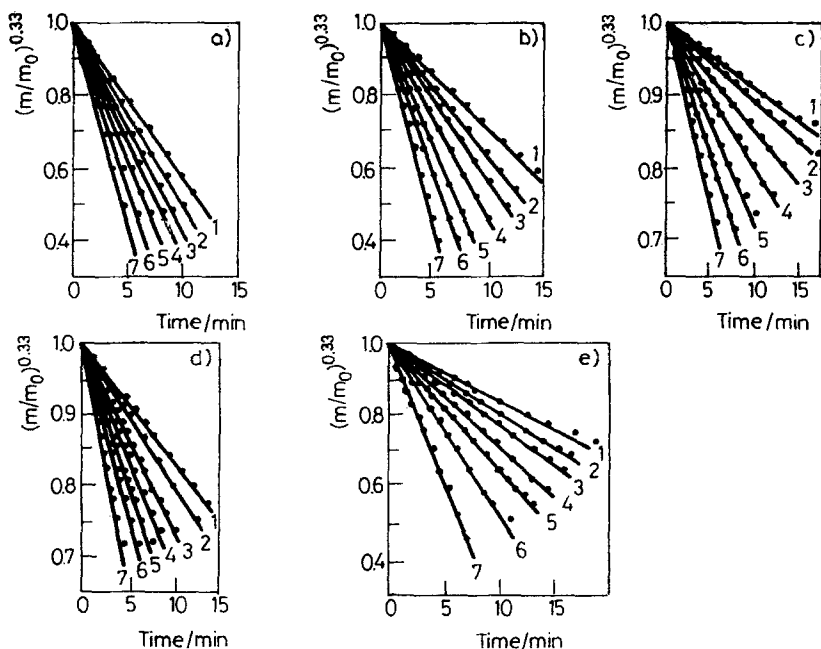Fig. 4 X-ray diffraction patterns of $Fe(OH)_3$-$Co(OH)_2$ mixtures calcined at 600°C (a) and 400°C (b)

Fig. 5 $(m/m_0)^{0.33}$ vs. time at various temperatures of pure $Fe(OH)_2$ (a) and mixed with $0.2Co^{2+}$ (b), $1Co^{2+}$ (c) and $1.5Co^{2+}$ ions (d), curve (e) of pure $Co(OH)_2$. [175°C (1), 200°C (2), 225°C (3), 250°C (4), 275°C (5), 300°C (6) and 350°C (7)]

mixing ratio of $x = 1.0$. The most intense lines corresponding to the spinel lattice structure are at $d(Å) = 2.94, 2.51, 2.09, 1.61$ and 1.48 corresponding to $I/I_o = 29.8, 100.0, 24.0. 21.9$ and 32.2. These results are found in agreement with results obtained by Goldstein and Tseung [24]. It is worthnoting that the diffraction lines of cobalt ferrite spinel are detected in the mixed samples calcined at 400°C (Fig. 4, curve b). The infrared absorption spectra of the thermal products of $Fe(OH)_3–Co(OH)_2$ mixtures calcined at 600°C are shown in Fig. 3, (curves c and d) correspond to $x = 0.2, 1$ and 1.5, respectively. These curves indicate that the strong absorption band assigned at 590 and 390 cm^{-1} corresponded to the ferrite spinel [25].

Kinetics and isothermal decomposition

TG and DTA results indicated a suitable temperature range of 175°–350°C for kinetics of isothermal decomposition studies of pure and mixed hydroxides. It has been determined that, in general, the decomposition curves are of the usual sigmodial type. This character indicates that the autocatalytic processes of nucleation and growth commonly encountered in solids. It is to be noted that the sigmodial character of the isothermal curves increases with the increase of the

temperature of thermolysis. Britton *et al.* [26] have proposed an equation for such decomposition process as follows:

$$(m/m_o)^{0.33} = Kt + b \qquad (1)$$

where m_o is the weight of total volatile compounds in the initial sample, m is the weight of volatile compounds remaining at time t, K is the velocity constant and b is a constant. Plotting $(m/m_o)^{0.33}$ against t gives straight lines as indicated in Fig. 5, the slope of which gives the specific velocity constant K. On plotting log K against l/T according to Arrhenius equation, other straight lines are obtained represented in Fig. 6. The values of activation energies are found 15, 24, 28, 22 and 25 kJ·mol^{-1} for pure Fe(OH)$_3$ and Fe(OH)$_3$ mixed with cobalt ions ($x = 0.2$, 1 or 1.5) and pure Co(OH)$_2$ respectively. It can be concluded that the rate and the activation energy of the thermal decomposition of Fe(OH)$_3$ are strongly affected in presence of cobalt ions. It is known, the thermal decomposition process is influenced by lattice defects (anionic and cationic vacancies), interstitial ions and electronic defects (free electrons and positive holes). In many cases these defects determine the occurrence of the elementary steps in the thermal decomposition process and hence their concentration may be of substantial importance. Therefore, the introduction of Co^{2+} into Fe$_2$O$_3$ lattice positions during its ther-
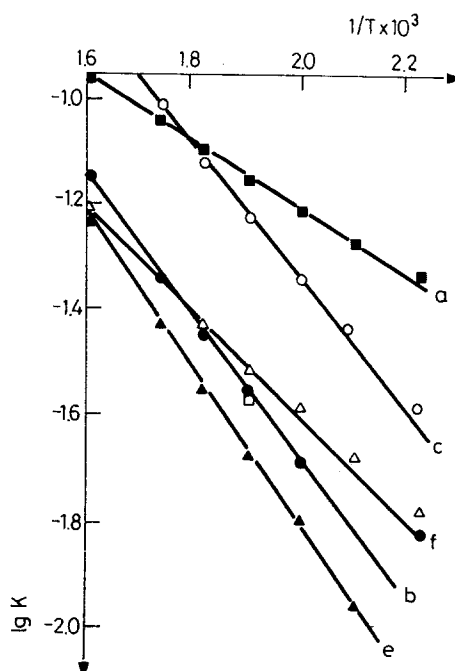

Fig. 6 Arrhenius plot of the thermal decomposition of iron hydroxide (*a*), cobalt hydroxide (*b*) and iron hydroxide mixed with 0.2Co^{2+} (*c*), 1Co^{2+} (*d*) and 1.5Co^{2+} ions (*e*)

molysis should create holes. From the results of X-ray diffraction, cobalt oxide has the form Co_3O_4 in the temperature range $250°$–$600°C$. Consequently, this spinel structure provided doping in the forms of CoO and Co_2O_3. However, only CoO should affect the thermal decomposition of $Fe(OH)_3$ via the following doping mechanism:

$$CoO \rightarrow Co \mid Fe \; |' + Fe_2O_3 + \mid e \mid^{\bullet} \qquad (2)$$
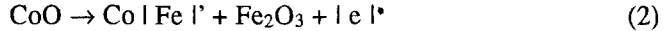
where $Co \mid Fe \; |'$ represents Co^{2+} ion substituted Fe^{3+} ion in its normal lattice site position and $\mid e\mid$ refers to a hole. The creation of holes within the lattice of Fe_2O_3 (*n*-type semiconductor) should retard its decomposition rate via the

$$\mid e \mid^{\bullet} + e \rightarrow null \qquad (3)$$

Also, it is observed that the retardation effect depends on the concentration of cobalt ions. Thus the mixed samples should require a higher energy to achieve thermal decomposition which is in accordance with the values of activation energy here obtained.

Electrical conductivity measurements

The electrical conductivity variation accompanying the thermal decomposition process of pure and mixed samples was carried out and plotted in Fig. 7, (curve a) shows an increase in σ values with the temperature increase reaching maximum. This maximum followed by a decrease in σ values up to temperature of $394°C$ then σ increases again. The first increase in σ values may due to the decomposition of $Fe(OH)_3$ into γ-Fe_2O_3 accompanying with the increase in charge carriers. The decrease in σ values reaching minimum seems to be interest. It was reported that [14] above $250°C$, a solid solution can be formed between Fe_3O_4 and γ-Fe_2O_3 expressed as

$$Fe^{3+}(\square_x Fe^{2+}_{1-3x} Fe^{3+}_{1+2x}) \, O_4^{2-}$$
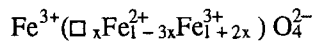
where $\square$ is a cation vacancy, and x degree of oxidation ($x = 1/3$ when oxidation is total). Therefore, the decrease in conductivity on increasing the heating temperature would be attributed to the decrease in the electron exchange process between Fe^{2+} in Fe_3O_4 and Fe^{3+} generated on grain [27, 28]. The effect of Co^{2+} additions on the conductivity variation of $Fe(OH)_3$ during its decomposition is shown in Fig. 7, curves (*b, c* and *d*). Analysis of the plot of $\log \sigma$ *vs.* $1/T$ must include consideration of the physical factors involved in the transformation of a compound (formed during a chemical reaction) in the amorphous phase of fusion layers to large crystallites, through the probable intermediate stages, such as the formation of a fine network of grain boundaries and subsequent consolidation, and the for-
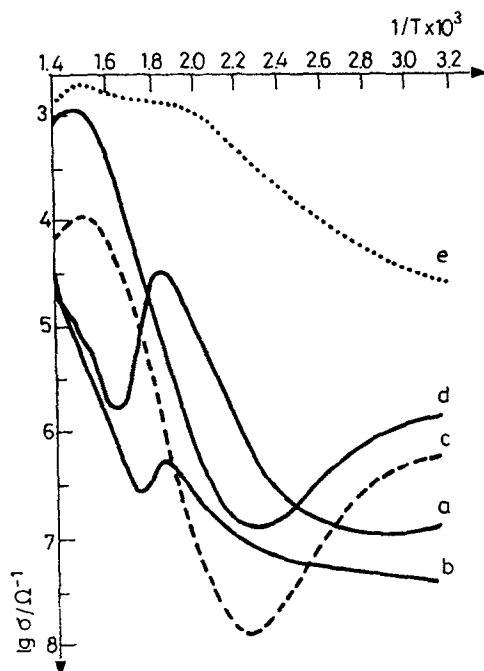
Fig. 7 Log σ *vs.* $1/T$ of pure $Fe(OH)_3$ (*a*), pure $Co(OH)_2$ (*e*) and $Fe(OH)_3$ mixed with $0.2Co^{2+}$ (*b*), $1Co^{2+}$ (*c*) and $1.5Co^{2+}$ ions (*d*)

mation of defects and subsequent annealing of such defects. However, the obtained results can be concluded as follows:

(i) Addition of cobalt hydroxide ($x = 0.2$) the result in curve (*b*) shows a similar behaviour to pure $Fe(OH)_3$ whereas the values of the conductance are less than that obtained in case of pure sample. On the other hand, the maximum conductance of $Fe(OH)_3$ obtained around 250°C shifted to higher temperature. This confirms the result of thermal analysis in which the presence of Co^{2+} retarded the thermal decomposition of ferric hydroxide. Moreover, according to Eq. (3), the decrease in σ values can be understood on the basis of the neutralization of holes within n-type semiconductor.

(ii) On increasing the cobalt concentration ($x = 1$ or 1.5) it appears that the conductance behaviour is completely changed. On heating of these samples, the electrical conductivity decreases to minimum values around 200° and 180°C for $x = 1$ and $x = 1.5$ respectively. This minimum is followed by a continuous increase in σ values with increasing the temperature up to 440°C, then it turns to decrease again. The minimum conductance may be attributed to the decrease of charge carriers during the decomposition of both hydroxides. The steep increase in σ values on increasing the heating temperature may be explained via the existence of dif-

ferent valencies. The presence of Co^{2+}/Co^{3+} ratio together with Fe^{2+}/Fe^{3+} facilitate the electron hopping between Fe^{2+} and Co^{3+}. The process should go forward until oxidation of all Fe^{2+} in Fe_3O_4. The decrease in the conductance above the temperature of 440°C is probably due to the formation of cobalt ferrite spinel.

(iii) A comparison of the conductance of pure $Co(OH)_2$, (curve d) with mixed samples during their thermolysis shows that cobalt oxide is responsible for such increase in the electrical conductivity of mixed samples. These results should play a deceive role in the catalytic activity of Fe_2O_3-Co_3O_4 system.

Conclusions

These are the main conclusions that can be derived from the results obtained:

1. The presence of Co^{2+} retarded the thermal decomposition of $Fe(OH)_3$ as well as the transformation of γ-Fe_2O_3 to α-Fe_2O_3. The consumption of holes created during the thermolysis responsible for such retardation. The activation energies calculated from the kinetics of isothermal decomposition in agreement with this suggestion.

2. Fe_2O_3 and Co_3O_4 reacted to form cobalt ferrite, $CoFe_2O_4$ at a temperature starting at 400°C, the cobalt ferrite produced remains thermally stable even when heated to 600°C.

3. The continuous measurement of the electrical conductivity during thermal decomposition of mixed samples indicated that the presence of Co^{2+} ($x = 0.2$) decreases the electrical conductance via the consumption of holes whereas the formation of spinel ($x = 1$ or 1.5) accompanied with a continuous increase in the (conductance value). This increase attributed to the presence of mixed valencies i.e. Fe^{2+}/Fe^{3+} and Co^{2+}/Co^{3+} which facilitate the electron hopping between Fe^{2+} and Co^{3+} cations.

References

1 V. V. Boldyrev, M. Bulens and B. Delmun, The control of the reactivity of solids, Elsevier, Amsterdam 1979.
2 B. L. Kuglar and J. W. Gryder, J. Catal., 44 (1979) 126.
3 T. Uenatsu, K. Inamura, K. Hirari and H. Hashimoto, J. Catal., 45 (1976) 68.
4 A. C. C. Tseung and J. R. Goldstein, J. Mat. Sci., 7 (1972) 1383.
5 R. R. Jaran and P. A. Sermon, J. Chem. Soc. Faraday Trans. I, 81 (1985) 2577.
6 A. A. Said, E. A. Hassan and K. M. Abd El-Salaam, Surf. Technol., 20 (1983) 123.
7 J. V. Smith, Ed., X-ray Powder Data File, American Soc. for Testing Materials, Philadelphia 1960.
8 C. Barriga, P. Lavela, J. Morales and J. Tirado, J. Coll. Interface Sci., 138 (1990) 565.
9 B. Gillot, F. Bouton, F. Chassagneux and A. Rousset, J. Solid State Chem., 33 (1980) 245.
10 B. Gillot, R. M. Benloucif and A. Rousset, ibid., 39 (1981) 329.
11 B. Gillot, Mater. Res. Bull., 13 (1978) 783.
12 B. Gillot, A Rousset and G. Dupre, ibid., 25 (1978) 263.
13 B. Gillot, F. Jemmal and A. Rousset, J. Solid State Chem., 50 (1983) 138.

14 B. Gillot, R. M. Benloucif and F. Jemmal, J. Mat. Sci., 19 (1984) 3806.
15 H. Takai and S. Shiba, J. Phys. Soc. Jpn., 21 (1966) 1255.
16 M. Figlarz, J. Guenot and J. N. Tournemolle, J. Mat. Sci., 19 (1974) 772.
17 J. T. Richardson and L. W. Vernson, J. Phys. Chem., 62 (1958) 1153.
18 H. De Bie and P. Doyen, Cobalt, 15 (1962) 3.
19 G. A. El-Shobaky, N. Ghoneim and I. F. Hewaidy, Thermochim. Acta, 5 (1982) 105.
20 R. A. Nyquist and R. O. Kagel, Infrared Spectra of Inorganic Compounds, Academic Press, New
   York and London 1971.
21 G. A. El-Shobaky, N. Ghoneim, I. F. Hewaidy and I. Morsi, Thermochim. Acta, 61 (1983) 107.
22 J. M. Jimenez-Mateos, J. Morales and J. L. Tirado, React. Solids, 7 (1989) 235.
23 B. Gillot and A. Rousset, J. Solid State Chem., 65 (1986) 322.
24 J. R. Goldstein and C. C. Tseung, J. Catal., 32 (1974) 33.
25 R. D. Waldron, Phys. Rev., 99 (1955) 1727.
26 H. T. S. Britton, S. J. Gregg and G. W. Winsor, Trans. Faraday Soc., 48 (1952) 63.
27 B. Gillot, R. M. Benloucif and A. Rousset, Phys. Status Solid (a), 65 (1981) 205.
28 F. Chassagneux and A. Rousset, J. Solid State Chem., 16 (1976) 161.

Zusammenfassung — Mittels TG, DTA und der Kinetik von Messungen der isothermen Zersetzung und der elektrischen Leitfähigkeit wurde die Zersetzung von $Fe(OH)_3$ in reinem Zustand und vermengt mit $Co(OH)_2$ untersucht. Die thermischen Produkte wurden mittels Röntgendiffraktion und IR-Spektroskopie charakterisiert. TG und DTA zeigen, daß die Zersetzung von Eisen(III)-hydroxid und die Bildung von -Fe_2O_3 durch Gegenwart von Co^{2+} verzögert wird. Die Zersetzungskinetik zeigt, daß die Mischproben mehr Energie für die Thermolyse benötigen. Die Untersuchung der thermischen Produkte zeigt die Bildung von Cobaltferrit bei Zusatz von $x=1$ oder 1,5 Cobalthydroxid. Die elektrische Leitfähigkeit nimmt bei der thermischen Zersetzung in Gegenwart von niedrigen Co^{2+}-Konzentrationen ($x=0.2$) durch Verbrauch der bei der Thermoanalyse geschaffenen Löcher ab. Das monotone Ansteigen der -Werte bei steigender Co^{2+}-Konzentration stimmt mit dem Überspringen von Elektronen zwischen Fe^{2+} und Co^{3+} überein.