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Institute of Nuclear Energetics¹) (a) and Institute of General and Inorganic Chemistry²) (b), Bulgarian Academy of Sciences, Sofia

Mössbauer Study of the Formation of Solid Solutions in the α -Fe₂O₃-Al₂O₃ System

By

T. TOMOV (a), D. KLISSURSKI (b), and I. MITOV (b)

The formation of solid solutions of α -Fe₂O₃ and Al₂O₃ at temperatures ranging from 80 to 950 °C is studied by Mössbauer spectroscopy, DTA, and specific surface area measurements. In the Mössbauer spectrum, a doublet is observed up to about 330 °C. At higher temperatures, a transition to a six-line spectrum is observed. The temperature of this transition increases with increasing Al₂O₃ content which is indicative of the retardation of the crystallization process. This is confirmed by DTA data. The solubility limit of Al₂O₃ in α -Fe₂O₃ as determined by measurements of the effective internal magnetic field values is $\approx 10 \text{ mol}\%$ Al₂O₃.

Методами Мессбауеровской спектроскопии, ДТА и измерением удельной поверхности исследовано образование твердых растворов α -Fe₂O₃ в Al₂O₃ в температурном интервале 80 до 950 °C. До температур 330 °C наблюдается дублетный спектр, который переходит в секстетный при более высоких температурах. Температура перехода растет с увеличением содержания Al₂O₃, что указывает на замедление процессов рекристаллизации. Это было подтверждено также данными ДТА. Граница растворимости Al₂O₃ в α -Fe₂O₃, определенной по данным измерения эффективного внутренного магнитного поля составляет $\approx 10 \text{ mol}_{0}^{\circ}$ Al₂O₃.

1. Introduction

The close values of the ionic radii of Fe^{3+} and Al^{3+} favour the formation of solid solutions of their oxides. The Al_2O_3 - Fe_2O_3 system is of special interest with respect to the preparation of catalysts for ammonia synthesis. Irrespective of the fact that this system has been the subject of many investigations [1 to 6], the data on the concentration limits of solubility are very contradictory.

The present paper contains results of a more detailed study of the interactions between Fe_2O_3 and Al_2O_3 in the temperature range 80 to 950 °C by Mössbauer spectroscopy.

2. Experimental

Samples of ferric and aluminium hydroxides and their mixtures were prepared by precipitation and coprecipitation of iron and aluminium nitrates using a 12.5% solution of NH₄OH at 20 °C and pH = 9. The sample compositions expressed as oxides are given in Table 1.

The Mössbauer spectra were taken at room temperature, the source used being Co^{57} in Pd. The powder samples (50 mg/cm²) were placed in lucite sample holders. The constant acceleration spectrometer was calibrated with α -Fe and the center of its

^{1) 1040} Sofia, Bulgaria.

²) 1113 Sofia, Bulgaria.

Compositions of coprecipitated ferric and aluminium hydroxides (expressed as oxides)									
sample No.	1	2	3	4	5	6	7	8	9
Al_2O_3 content (mol%)	0	100	1.0	2.9	4.8	9.2	13.2	16.8	33.6

spectrum is used as a reference point for isomer shift measurements. The endothermic and exothermic processes taking place during heating of the samples were recorded by a SUEM-676 DTA apparatus at temperatures ranging between 20 and 1300 °C with a heating rate of 6 K/min. The infrared spectra were taken with a Carl-Zeiss Jena VP-2 spectrometer by pressing the samples in KBr pellets.

The specific surface areas were measured by a modified BET method [8] for surfaces above $2 \text{ m}^2/\text{g}$ and by the BET method, whereas low-temperature krypton adsorption was applied to surface areas smaller than $2 \text{ m}^2/\text{g}$ [9]. Iron(III) and coprecipitated iron(III)-aluminium(III) hydroxides were heated in the temperature range 80 to 950 °C for 4 h in air.

3. Results and Discussion

Differential thermal analysis (DTA) and thermogravimetric (TG) analysis curves of ferric hydroxide, aluminium hydroxide, and some of their mixtures are presented in Fig. 1. The DTA curves show the endothermal effects of dehydration at 160 to 180 °C and the exothermal effects of α -Fe₂O₃ crystallization which are more pronounced at 400 to 670 °C depending on the amount of aluminium compound in the system. Obviously, this compound increases the stability range of the amorphous component of the system. The effects observed with dehydration of aluminium hydroxide are in agreement with the results of a previous study [10].

The specific surface areas substantially change during heating. The values for the specific surface areas of some of the initial samples heated at different temperatures for 4 h are given in Table 2.

Table 2

Data for the specific surface areas of the initial samples after heating for 4 h at different temperatures

temperature of heating (°C)	specific surface areas (m^2/g) corresponding to Al_2O_3 content (mol%)						
	0	4.8	13.2	33.6			
80	229	260	238	289			
180	262	272	274	305			
220	221	265	273	282			
400	65	123	213	261			
500	34.2	47	82	129			
600	4.9	19.3	40	81.5			
800	0.29	2.18	9	16.2			
950	0.22	0.26	0.9	3.2			

The specific surface areas increase with increasing Al_2O_3 content. This is indicative of the structurizing effect of the latter. The decrease in the specificsur face area with

Table 1



Fig. 1. DTA and TG curves of: a) sample 1; b) 2; c) 5; d) 7; e) 9; temperatures in $^{\circ}C$

increasing temperature of heat-treatment shows a considerable intensity of recrystallization and sintering at temperatures above 400 °C.

The results of the Mössbauer study are given in Fig. 2 and Table 3. The spectrum of ferric hydroxide shows a quadrupole doublet. During the heating, the gel is partially dehydrated which results in a change in the Mössbauer spectrum. The spectrum of ferric hydroxide heated at 330 °C represents two superimposed spectra (a doublet and a six-line spectrum). After heat treatment up to 400 °C the sample has the spectrum of α -Fe₂O₃. The effective internal magnetic field determined by the spectrum of this sample has a lower value ($H_{\rm eff} = 512.7 \pm \pm 1.4$ kOe).

At heating temperatures above 600 °C the internal magnetic field is $H_{\rm eff} = 518$ kOe, i.e. the structure obtained has a $H_{\rm eff}$ value characteristic of α -Fe₂O₃ (II).

The lower H_{eff} values for samples heated at relatively low temperatures can be ascribed to the presence of structural water [12] or to the formation of a defect structure at these temperatures [13]. With increasing temperature of heat treatment, crystallization processes take place, leading to the stabilization of the magnetic



Fig. 2. Mössbauer spectra of sample 1 heat-treated at (1) T = 80, (2) 330, (3) 400 °C



Fig. 3. Dependence of effective internal magnetic field on the temperature of heat treatment of the samples: (1) sample 1, (2) 5, (3) 7, (4) 9

structure. By means of a gravimetric method it was found that the initial amorphous substance detected by X-ray analysis corresponds to the composition $Fe_2O_3 \cdot H_2O$ and, more precisely, to $Fe_2O_3 \cdot 1.2 H_2O$. The infrared spectra indicate that an amorphous Fe^{3+} hydroxide is not a hydrated iron oxide but rather a Fe^{3+} hydroxide. The Mössbauer study (the IS and QS values) confirmed the presence of X-ray amorphous Fe^{3+} hydroxide [14, 15]. Decomposition of the hydroxide upon thermal treatment leads to the formation of hematite.

The Mössbauer spectra of Fe(III)-Al hydroxides also represent quadrupole doublets. The values of isomer shift (IS) (determined on their basis) for the Fe³⁺ hydroxide and the combined hydroxides are close, which indicates a negligible difference in the electron densities in the region of the iron nucleus of the samples investigated. An increase in the quadrupole splitting (QS) with increasing heating temperature and amount of the aluminium compound was observed. The change in QS indicates a disturbed symmetry of the surrounding of the iron nucleus due to the effect of the second component in the system (Al³⁺ and Fe³⁺ differ in their electronegativity) and to partial dehydration. The spectrum changes from a doublet to a six-line form in the case of combined hydroxides at higher temperatures. It is worth noting that the larger the amount of aluminium component in the system, the higher the temperature of this transition (Table 3). This was also confirmed by DTA data.

The effective magnetic field changes as for sample 1 (α -Fe₂O₃). Nevertheless, the final values of H for samples containing Al₂O₃ are lower than H_{eff} for α -Fe₂O₃ (Fig. 3). There is qualitative agreement between this result and the results obtained in the study of some minerals [1, 2].

The change in $H_{\rm eff}$ is caused by the formation of a solid solution of Al_2O_3 in α -Fe₂O₃. In the solubility limits aluminium oxide is completely consumed for the formation of the solid solution at heating temperatures above 800 °C. For samples with 9.2 to $16.2 \text{ mol}\% Al_2O_3$ $H_{\rm eff} = 509 \text{ kOe}$. The preservation of a constant H value after a certain Al_2O_3 content indicates the restricted solubility of Al_2O_3 in the system under consideration.

It should be noted that in considering the character and extent of the change in H_{eff} one should take into account not only the exchange interactions in the ion but also its bonds with the ions from its surrounding, the type of chemical bond, etc. During the formation of a solid solution and the replacing of a magnetic ion by a nonmagnetic

Table 3

tempera- ture of heating (°C)	sample 1	sample 5	sample 7	sample 9
80				$\begin{array}{l} \text{doublet} \\ \text{IS} &= 0.342 \\ \text{QS} &= 0.70 \end{array}$
180	$egin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{l} \text{doublet} \\ \text{IS} \ = \ 0.347 \\ \text{QS} \ = \ 0.69 \end{array}$	$egin{array}{llllllllllllllllllllllllllllllllllll$	$egin{array}{l} { m doublet} \ { m IS} = 0.342 \ { m QS} = 0.72 \end{array}$
330	$\begin{array}{l} \text{doublet} \\ \text{IS} = 0.35 \\ \text{QS} = 0.7 \\ \text{six-line spectrum} \\ \text{IS} = 0.37 \\ \text{QS} = -0.1 \\ H_{\text{eff}} = 503 \end{array}$	_	_	_
400	six-line spectrum IS = 0.369 QS = -0.105 $H_{\rm eff} = 512.7$	$\begin{array}{l} \text{doublet} \\ \text{IS} &= 0.35 \\ \text{QS} &= 0.7 \\ \text{six-line spectrum} \\ \text{IS} &= 0.362 \\ \text{QS} &= -0.105 \\ H_{\text{eff}} &= 503.6 \end{array}$	$egin{array}{l} { m doublet} \ { m IS} \ = \ 0.347 \ { m QS} \ = \ 0.71 \end{array}$	$\begin{array}{l} \text{doublet} \\ \text{IS} \ = \ 0.347 \\ \text{QS} \ = \ 0.83 \end{array}$
600	six-line spectrum IS = 0.369 QS = -0.102 $H_{eff} = 518.6$	six-line spectrum IS = 0.362 QS = -0.107 $H_{\rm eff} = 512.4$	${ m six-line \; spectrum} \ { m IS} = 0.362 \ { m QS} = -0.11 \ { m H_{eff}} = 506.5$	$\begin{array}{l} \text{doublet} \\ \text{IS} &= 0.322 \\ \text{QS} &= 0.8 \\ \\ \text{six-line spectrum} \\ \text{IS} &= 0.352 \\ \text{QS} &= -0.1 \\ H_{\text{eff}} &= 504 \end{array}$
800	six-line spectrum	six-line spectrum	six-line spectrum	six-line spectrum
950	$H_{\rm eff}=518$	$H_{\rm eff}=513.5$	$H_{ m eff} = 509$	$H_{\rm eff}=509$

Basic characteristics of the Mössbauer spectra of samples heated for 4 h at different temperatures $(T_{\rm h})$

18 (mm/s), QS (mm/s), H_{eff} (kOe).

one, the chain of exchange interactions will be interrupted, which, of course, would produce a change in $H_{\rm eff}$. The replacement of Fe³⁺ by Al³⁺ can affect $H_{\rm eff}$ due to the change in volume of the elementary cell (for Al³⁺ r = 0.57 Å, whereas for Fe³⁺ r = 0.67 Å), i.e. due to the increase in the electron density. The change in $H_{\rm eff}$ of samples with different contents of aluminium oxide was found to be negligible. The decrease in $H_{\rm eff}$ is caused mainly by the magnetic rarefaction of the system and by disturbance of the cooperative interactions. The change in $H_{\rm eff}$ is observed up to 9.2 mol% of Al₂O₃. A little higher value (up to $\approx 13 \,\mathrm{mol}\% \,\mathrm{Al}_2\mathrm{O}_3$) has been found on the basis of X-ray analysis. The data obtained by both methods confirm the restricted solubility of Al_2O_3 in α -Fe₂O₃. It was also found that under the experimental conditions of these studies solid solutions are formed at an appropriate rate at temperatures above 800 °C.

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